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(54) Title: INORGANIC PARTICLE-COATED GLASS FIBER STRANDS AND PRODUCTS INCLUDING THE SAME			
(57) Abstract The present invention provides glass fiber strands coated and impregnated with greater than 20 weight percent of inorganic particle fillers which are useful for reinforcing composites.			

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**INORGANIC PARTICLE-COATED GLASS FIBER
STRANDS AND PRODUCTS INCLUDING THE SAME**

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Cross Reference to Related Applications

This patent application is a continuation-in-part application of U.S. Serial No. 09/034,056 of B. Novich et al. entitled "Inorganic Particle-Coated Glass Fiber Strands and Products Including the Same" filed March 3, 1998.

- 10 This patent application is related to U.S. Patent Application Serial No. _____ of B. Novich et al. entitled "Methods for Inhibiting Abrasive Wear of Glass Fiber Strands", which is a continuation-in-part application of U.S. Application Serial No. 09/034,078 filed March 3, 1998; U.S. Patent Application Serial No. _____ of B. Novich et al. entitled "Glass Fiber Strands Coated
- 15 With Thermally Conductive Inorganic Solid Particles and Products Including the Same", which is a continuation-in-part application of U.S. Application Serial No. 09/034,663 filed March 3, 1998; U.S. Patent Application Serial No. _____ of B. Novich et al. entitled "Impregnated Glass Fiber Strands and Products Including the Same", which is a continuation-in-part application of
- 20 U.S. Application Serial No. 09/034,077 filed March 3, 1998; U.S. Patent Application Serial No. _____ of B. Novich et al. entitled "Inorganic Lubricant-Coated Glass Fiber Strands and Products Including the Same", which is a continuation-in-part application of U.S. Application Serial No. 09/034,525 filed March 3, 1998; and U.S. Patent Application Serial No. _____ of B. Novich
- 25 et al. entitled "Glass Fiber-Reinforced Laminates, Electronic Circuit Boards and Methods for Assembling a Fabric", which is a continuation-in-part application of U.S. Application Serial No. 09/130,270 filed August 6, 1998, each of which has been filed concurrently with the present application.

30

Field of the Invention

This invention relates generally to coated glass fiber strands for reinforcing composites and, more specifically, to glass fiber strands coated with greater than 20 weight percent of solid filler particles.

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Background of the Invention

In thermosetting molding operations, good "wet-through" (penetration of the polymeric matrix material through the mat) and "wet-out" (penetration of the polymeric matrix material through the individual bundles or strands of fibers in the mat) properties are desirable. In contrast, good dispersion properties are of predominant concern in typical thermoplastic molding operations.

For improving resin impregnation, Japanese Patent Application No. 9-208,268 discloses a cloth having yarn formed from glass fibers coated immediately after spinning with starch or a synthetic resin and 0.001 - 20.0 weight percent of inorganic solid particles such as colloidal silica, calcium carbonate, kaolin and talc having average particles sizes of 5 to 2000 nanometers (0.05 to 2 micrometers). In paragraph 13 of the Detailed Description of the Invention, it is disclosed that such coatings having more than 20 weight percent inorganic solid particles cannot be applied to the glass fiber. To improve penetration of resin between glass reinforcement fibers during formation of a composite, U.S. Patent No. 3,312,569 discloses adhering particles of alumina to the surfaces of the glass fibers. However, the Mohs' hardness values of alumina and silica are greater than about 9 and about 7¹, respectively, which can cause abrasion of softer glass fibers.

Soviet Union No. 859400 discloses an impregnating composition for manufacturing laminates of glass fiber cloth, the composition containing an alcoholic solution of phenol-formaldehyde resin, graphite, molybdenum disulphide, polyvinyl butyral and surfactant. Volatile alcoholic solvents are not desirable for glass fiber production applications.

¹ See R. Weast (Ed.), Handbook of Chemistry and Physics, CRC Press (1975) at page F-22 and H. Katz et al. (Ed.), Handbook of Fillers and Plastics, (1987) at page 28, which are hereby incorporated by reference.

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To enhance, reduce or modify frictional characteristics of a composite, U.S. Patent No. 5,217,778 discloses a dry clutch facing including a composite yarn of glass fibers, metallic wire and polyacrylonitrile fibers which are impregnated and coated with a heat curable cement or binder system. The
5 binder can include friction particles such as carbon black, graphite, metal oxides, barium sulfate, aluminum silicate, ground rubber particles, ground organic resins, polymerized cashew nut oil, clay, silica or cryolite (see col. 2, lines 55-66).

There is a need for coatings which inhibit abrasion and breakage of
10 glass fibers, which are compatible with a wide variety of polymeric matrix materials and which include less expensive components than conventional coating formulations.

Summary of the Invention

15 The present invention provides a coated fiber strand comprising at least one glass fiber at least partially coated with a dried residue of an aqueous sizing composition comprising greater than 20 weight percent on a total solids basis of inorganic solid particles which have a hardness which does not exceed a hardness of the at least one glass fiber.

20 Another aspect of the present invention is a coated fiber strand comprising at least one glass fiber, the strand having (1) a primary layer of a dried residue of a sizing composition applied to at least a portion of surfaces of at least one glass fiber and (2) a secondary layer of an aqueous secondary coating composition applied over at least a portion of the primary layer, the
25 secondary coating composition comprising greater than 20 weight percent on a total solids basis of inorganic solid particles.

Yet another aspect of the present invention is a coated fiber strand comprising at least one glass fiber, the strand having (1) a primary layer of a dried residue of a sizing composition applied to at least a portion of surfaces

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of the at least one glass fiber; (2) a secondary layer of a secondary coating composition applied over at least a portion of the primary layer, the secondary coating composition comprising a polymeric material; and a tertiary layer comprising greater than 20 weight percent on a total solids basis of powdered
5 inorganic solid particles applied over at least a portion of the secondary layer.

Another aspect of the present invention is a reinforced polymeric composite comprising: (a) a coated fiber strand comprising at least one glass fiber at least partially coated with a dried residue of an aqueous sizing composition comprising greater than 20 weight percent on a total solids basis
10 of inorganic solid particles which have a hardness which does not exceed a hardness of the at least one glass fiber; and (b) a polymeric matrix material.

Yet another aspect of the present invention is a fabric comprising a coated fiber strand comprising a coated fiber strand comprising at least one glass fiber at least partially coated with a dried residue of an aqueous sizing composition comprising greater than 20 weight percent on a total solids basis
15 of inorganic solid particles which have a hardness which does not exceed a hardness of the at least one glass fiber.

Another aspect of the present invention is an electronic support comprising: (a) a fabric comprising a coated fiber strand comprising at least
20 one glass fiber at least partially coated with a dried residue of an aqueous sizing composition comprising greater than 20 weight percent on a total solids basis of inorganic solid particles which have a hardness which does not exceed a hardness of the at least one glass fiber; and (b) a layer of a polymeric matrix material applied over at least a portion of the fabric.

25 Another aspect of the present invention is an electronic circuit board comprising: (a) an electronic support comprising: (i) a fabric comprising coated fiber strand comprising at least one glass fiber at least partially coated with a dried residue of an aqueous sizing composition comprising greater than 20 weight percent on a total solids basis of inorganic

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solid particles which have a hardness which does not exceed a hardness of the at least one glass fiber; and (ii) a layer of a polymeric matrix material applied over at least a portion of the fabric; and (b) an electrically conductive layer positioned adjacent to selected portions of selected sides of the

5 electronic support.

Still another aspect of the present invention is an electronic support comprising: (a) a first composite layer comprising: (i) a fabric comprising a coated fiber strand comprising at least one glass fiber at least partially coated with a dried residue of an aqueous sizing composition comprising greater

10 than 20 weight percent on a total solids basis of inorganic solid particles which have a hardness which does not exceed a hardness of the at least one glass fiber; and (ii) a layer of a polymeric matrix material applied over at least a portion of the fabric; and (b) a second composite layer different from the first composite layer.

15 Yet another aspect of the present invention is an electronic circuit board comprising: (a) an electronic support comprising: (i) a first composite layer comprising: (1) a fabric comprising coated fiber strand comprising at least one glass fiber at least partially coated with a dried residue of an aqueous sizing composition comprising greater than 20 weight percent on a

20 total solids basis of inorganic solid particles which have a hardness which does not exceed a hardness of the at least one glass fiber; and (2) a layer of a polymeric matrix material applied over at least a portion of the fabric; and (ii) a second composite layer different from the first composite layer; and (b) an electrically conductive layer positioned adjacent to selected portions of

25 selected sides of the first and/or second composite layers.

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Brief Description of the Drawings

The foregoing summary, as well as the following detailed description of the preferred embodiments, will be better understood when read in conjunction with the appended drawings. In the drawings:

5 Fig. 1 is a perspective view of a coated fiber strand having a primary layer of a dried residue of an aqueous sizing composition according to the present invention;

10 Fig. 2 is a perspective view of a coated fiber strand having a primary layer of a dried residue of a sizing composition and thereupon a secondary layer of an aqueous secondary coating composition according to the present invention;

15 Fig. 3 is a perspective view of a coated fiber strand having a primary layer of a dried residue of a sizing composition, a secondary layer of an aqueous secondary coating composition, and a tertiary layer thereupon according to the present invention;

 Fig. 4 is a top plan view of a composite according to the present invention;

 Fig. 5 is a top plan view of a fabric according to the present invention;

20 Fig. 6 is a cross-sectional view of an electronic support according to the present invention; and

 Figs. 7 and 8 are cross-sectional views of alternate embodiments of an electronic support according to the present invention.

Detailed Description of the Invention

25 The glass fiber strands of the present invention have a unique coating which not only inhibits abrasion and breakage of the fibers during processing but can provide good wet-through, wet-out and dispersion properties in formation of composites. Good thermal stability, good hydrolytic stability, good laminate strength, low corrosion and reactivity in the presence of high

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humidity, reactive acids and alkalies and compatibility with a variety of polymeric matrix materials, which can eliminate the need for heat cleaning prior to lamination, are other desirable characteristics which can be exhibited by the coated glass fiber strands of the present invention.

5 Another significant advantage of the coated glass fiber strands of the present invention is good processability in weaving and knitting. Low fuzz and halos, low broken filaments, low strand tension, high fiability and low insertion time are characteristics which can be provided by the coated glass fiber strands of the present invention to facilitate weaving and knitting and
10 consistently provide a fabric with few surface defects for printed circuit board applications.

Referring now to Fig. 1, wherein like numerals indicate like elements throughout, there is shown in Fig. 1 a coated fiber strand 10 comprising at least one glass fiber 12 or quartz fiber, according to the present invention.
15 Preferably the strand 11 comprises a plurality of glass fibers 12. As used herein, the term "strand" means one or more individual fibers. The term "fiber" means an individual filament. The fibers 12 have an average nominal fiber diameter greater than 5 micrometers, preferably greater than 7 micrometers, and more preferably greater than 9 micrometers.

20 The glass fibers 12 can be formed from any type of fiberizable glass composition known to those skilled in the art, including those prepared from fiberizable glass compositions such as "E-glass", "A-glass", "C-glass", "D-glass", "R-glass", "S-glass", and E-glass derivatives. As used herein, "E-glass derivatives" means glass compositions which include minor amounts
25 of fluorine and/or boron and preferably are fluorine-free and/or boron-free. Furthermore, as used herein, minor means less than about 1 weight percent fluorine and less than about 5 weight percent boron. Basalt and mineral wool fibers are examples of other glass fibers useful in the present invention. Preferred glass fibers are formed from E-glass or E-glass derivatives. Such

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compositions and methods of making glass filaments therefrom are well known to those skilled in the art and further discussion thereof is not believed to be necessary in view of the present disclosure. If additional information is needed, such glass compositions and fiberization methods are disclosed in K.

- 5 Loewenstein, The Manufacturing Technology of Glass Fibres, (3d Ed. 1993) at pages 30-44, 47-60, 115-122 and 126-135, and U.S. Patent Nos. 4,542,106 and 5,789,329, which are hereby incorporated by reference.

In addition to glass fibers, the coated fiber strand 10 can further comprise fibers formed from other fiberizable natural or man-made materials, such as non-glass inorganic materials, natural materials, organic polymeric materials and combinations thereof. As used herein, the term "fiberizable" means a material capable of being formed into a generally continuous filament, fiber, strand or yarn.

- Suitable non-glass inorganic fibers include ceramic fibers formed from silicon carbide, carbon, graphite, mullite, aluminum oxide and piezoelectric ceramic materials. Non-limiting examples of suitable animal and vegetable-derived natural fibers include cotton, cellulose, natural rubber, flax, ramie, hemp, sisal and wool. Suitable man-made fibers include those formed from polyamides (such as nylon and aramids), thermoplastic polyesters (such as polyethylene terephthalate and polybutylene terephthalate), acrylics (such as polyacrylonitriles), polyolefins, polyurethanes and vinyl polymers (such as polyvinyl alcohol). Non-glass fibers believed to be useful in the present invention and methods for preparing and processing such fibers are discussed at length in the Encyclopedia of Polymer Science and Technology, Vol. 6 (1967) at pages 505-712, which is hereby incorporated by reference. It is understood that blends or copolymers of any of the above materials and combinations of fibers formed from any of the above materials can be used in the present invention, if desired.

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The present invention will now be discussed generally in the context of glass fiber strands, although one skilled in the art would understand that the strand 10 can additionally include one or more of the non-glass fibers discussed above.

5 With continued reference to Fig. 1, in a preferred embodiment, fibers 12 of fiber strand 10 of the present invention are impregnated with a primary layer 14 of a dried residue of an aqueous sizing composition applied to at least a portion 17 of the surfaces 16 of the fibers 12 to protect the fiber surfaces 16 from abrasion during processing and inhibit breakage of the
10 fibers 12. Preferably the dried residue of the aqueous sizing composition is applied to the entire outer surface 16 or periphery of the fibers 12.

As used herein, in a preferred embodiment the terms "size", "sized" or "sizing" refer to the coating composition applied to the fibers immediately after formation of the fibers. In an alternative embodiment, the terms "size", "sized"
15 or "sizing" additionally refer to a coating composition (also known as a "finishing size") applied to the fibers after a conventional primary coating composition has been removed by heat or chemical treatment, i.e., the finishing size is applied to bare glass fibers incorporated into a fabric form.

The aqueous sizing composition comprises a plurality of inorganic solid
20 particles 18 positioned between or preferably adhered to the outer surfaces 16 of the fibers 12. As used herein, "solid" means a substance that does not flow perceptibly under moderate stress, has definite capacity for resisting forces which tend to deform it, and under ordinary conditions retains a definite size and shape. See Webster's Third New International Dictionary of the
25 English Language - Unabridged (1971) at page 2169. Furthermore, as used herein, the term "solid" includes both crystalline and non-crystalline materials.

The solid particles 18 preferably have a minimum average particle size 19 (equivalent spherical diameter) of at least 3 micrometers, preferably at least about 5 micrometers, and ranges from 3 to about 1000 micrometers,

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preferably from about 5 to about 1000 micrometers, and more preferably 10 to about 25 micrometers. Preferably, each of the solid particles has a minimum particle size of at least 3 micrometers, and preferably at least about 5 micrometers. It is also preferred that the minimum average particle size 19 of the solid particles correspond generally to the average nominal diameter of the glass fibers. It should be appreciated that particle sizes discussed above are preferred over the smaller particle sizes in part because they are generally less expensive and are easier to disperse. In addition, fabrics made with strands coated with the particles of the sizes as discussed above exhibit 10 better "wet through" and "wet out" characteristics when impregnated with a polymeric matrix material when compared to fabrics made with strands coated with smaller size particles.

The configuration or shape of the solid particles 18 can be generally spherical (such as beads, microbeads or solid hollow spheres), cubic, platy or 15 acicular (elongated or fibrous), as desired. For more information on suitable particle characteristics, see H. Katz et al. (Ed.), Handbook of Fillers and Plastics, (1987) at pages 9-10, which are hereby incorporated by reference. The solid particles 18 preferably maintain their minimum average particle size (equivalent spherical diameter) of at least 3 micrometers, and preferably at 20 least about 5 micrometers, and more particularly maintain their minimum particle size (equivalent spherical diameter) of at least 3 micrometers, and preferably at least about 5 micrometers, under processing conditions, such as the forces generated between adjacent fibers during weaving, roving and other processing operations, to maintain interstitial spaces between adjacent 25 fibers 23, 25. In other words, the solid particles preferably do not crumble or deform to a particle size less than their minimum particle size under typical glass fiber processing conditions, such as exposure to temperatures of up to about 25°C, and more preferably up to about 400°C.

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Glass fibers are subject to abrasive wear by contact with asperities of adjacent glass fibers and/or other solid objects or materials which the glass fibers contact during forming and subsequent processing, such as weaving or roving. "Abrasive wear", as used herein, means scraping or cutting off of bits of the glass fiber surface or breakage of glass fibers by frictional contact with particles, edges or entities of materials which are hard enough to produce damage to the glass fibers. See K. Ludema, Friction, Wear, Lubrication, (1996) at page 129, which is hereby incorporated by reference. Abrasive wear of glass fiber strands causes strand breakage during processing and surface defects in products such as woven cloth and composites, which increases waste and manufacturing cost.

To minimize abrasive wear, the solid particles have a hardness value which does not exceed, i.e., is less than or equal to, a hardness value of the glass fiber(s). The hardness values of the solid particles and glass fibers can be determined by any conventional hardness measurement method, such as Vickers or Brinell hardness, but is preferably determined according to the original Mohs' hardness scale which indicates the relative scratch resistance of the surface of a material. The Mohs' hardness value of glass fibers generally ranges from about 4.5 to about 6.5, and is preferably about 6. R. Weast (Ed.), Handbook of Chemistry and Physics, CRC Press (1975) at page F-22, which is hereby incorporated by reference. The Mohs' hardness value of the solid particles preferably ranges from about 0.5 to about 6. The Mohs' hardness values of several non-limiting examples of solid particles suitable for use in the present invention are given in Table A below.

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Table A

Solid particle material	Mohs' hardness (original scale)
boron nitride	about 2 ²
graphite	about 0.5-1 ³
molybdenum disulfide	about 1 ⁴
talc	about 1-1.5 ⁵
mica	about 2.8-3.2 ⁶
kaolinite	about 2.0-2.5 ⁷
gypsum	about 1.6-2 ⁸
calcite (calcium carbonate)	about 3 ⁹
calcium fluoride	about 4 ¹⁰
zinc oxide	about 4.5 ¹¹
aluminum	about 2.5 ¹²
copper	about 2.5-3 ¹³
iron	about 4-5 ¹⁴
gold	about 2.5-3 ¹⁵
nickel	about 5 ¹⁶
palladium	about 4.8 ¹⁷
platinum	about 4.3 ¹⁸
silver	about 2.5-4 ¹⁹

As mentioned above, the Mohs' hardness scale relates to the resistance of a material to scratching. The instant invention therefore

5 contemplates particles that have a hardness at their surface that is different

² K. Ludema, Friction, Wear, Lubrication, (1996) at page 27, which is hereby incorporated by reference.

³ Handbook of Chemistry and Physics at page F-22.

⁴ R. Lewis, Sr., Hawley's Condensed Chemical Dictionary, (12th Ed. 1993) at page 793, which is hereby incorporated by reference.

⁵ Hawley's Condensed Chemical Dictionary, (12th Ed. 1993) at page 1113, which is hereby incorporated by reference.

⁶ Hawley's Condensed Chemical Dictionary, (12th Ed. 1993) at page 784, which is hereby incorporated by reference.

⁷ Handbook of Chemistry and Physics at page F-22.

⁸ Handbook of Chemistry and Physics at page F-22.

⁹ Friction, Wear, Lubrication at page 27.

¹⁰ Friction, Wear, Lubrication at page 27.

¹¹ Friction, Wear, Lubrication at page 27.

¹² Friction, Wear, Lubrication at page 27.

¹³ Handbook of Chemistry and Physics at page F-22.

¹⁴ Handbook of Chemistry and Physics at page F-22.

¹⁵ Handbook of Chemistry and Physics at page F-22.

¹⁶ Handbook of Chemistry and Physics at page F-22.

¹⁷ Handbook of Chemistry and Physics at page F-22.

¹⁸ Handbook of Chemistry and Physics at page F-22.

¹⁹ Handbook of Chemistry and Physics at page F-22.

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from the hardness of the internal portions of the particle beneath its surface. More specifically, the surface of the particle can be modified in any manner well known in the art, including but not limited to coating, cladding or encapsulating the particle or chemically changing its surface characteristics

5 using techniques known in the art, such that the surface hardness of the particle is not greater than the hardness of the glass fibers while the hardness of the particle beneath the surface is greater than the hardness of the glass fibers. For example but not limiting the present invention, inorganic particles such as silicon carbide and aluminum nitride can be provided with a silica

10 carbonate or nanoclay coating. In addition, silane coupling agents with alkyl side chains can be reacted with the surface of many oxide particles to provide a "softer" surface.

Generally, solid particles 18 useful in the present invention can be formed from ceramic materials, metallic materials and mixtures thereof.

15 Suitable ceramic materials include metal nitrides, metal oxides, metal carbides, metal sulfides, metal borides, metal silicates, metal carbonates and mixtures thereof.

A non-limiting of a suitable metal nitride is boron nitride, which is the preferred inorganic material from which solid particles useful in the present

20 invention are formed. A non-limiting example of a useful metal oxide is zinc oxide. Suitable metal sulfides include molybdenum disulfide, tantalum disulfide, tungsten disulfide and zinc sulfide. Useful metal silicates include aluminum silicates and magnesium silicates. Suitable metallic materials include graphite, molybdenum, platinum, palladium, nickel, aluminum, copper,

25 gold, iron, silver and mixtures thereof. A useful mixture of alumina and silica is fly ash.

Preferably, the inorganic solid particles 18 are also solid lubricants. As used herein, "solid lubricant" means that the inorganic solid particles 18 have a characteristic crystalline habit which causes them to shear into thin, flat

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plates which readily slide over one another and thus produce an antifriction lubricating effect between the glass fiber surface and an adjacent solid surface, at least one of which is in motion. See R. Lewis, Sr., Hawley's Condensed Chemical Dictionary, (12th Ed. 1993) at page 712, which is
5 hereby incorporated by reference. Friction is the resistance to sliding one solid over another. F. Clauss, Solid Lubricants and Self-Lubricating Solids, (1972) at page 1, which is hereby incorporated by reference.

In a preferred embodiment, the solid lubricant particles have a lamellar structure. Particles having a lamellar or hexagonal crystal structure are
10 composed of sheets or plates of atoms in hexagonal array, with strong bonding within the sheet and weak van der Waals bonding between sheets, providing low shear strength between sheets. Friction, Wear, Lubrication at page 125, Solid Lubricants and Self-Lubricating Solids at pages 19-22, 42-54, 75-77, 80-81, 82, 90-102, 113-120 and 128, and W. Campbell "Solid
15 Lubricants", Boundary Lubrication; An Appraisal of World Literature, ASME Research Committee on Lubrication (1969) at pages 202- 203, which are hereby incorporated by reference. Inorganic solid particles having a lamellar fullerene (buckyball) structure are also useful in the present invention.

Non-limiting examples of suitable inorganic solid lubricant particles
20 having a lamellar structure include boron nitride, graphite, metal dichalcogenides, mica, talc, gypsum, kaolinite, calcite, cadmium iodide, silver sulfide and mixtures thereof. Preferred inorganic solid lubricant particles include boron nitride, graphite, metal dichalcogenides and mixtures thereof. Suitable metal dichalcogenides include molybdenum disulfide, molybdenum
25 diselenide, tantalum disulfide, tantalum diselenide, tungsten disulfide, tungsten diselenide and mixtures thereof.

Boron nitride particles having a hexagonal crystal structure are most preferred for use in the aqueous sizing composition. Boron nitride, zinc

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sulfide and montmorillonite particles also provide good whiteness in composites with polymeric matrix materials such as nylon 6,6.

Non-limiting examples of boron nitride particles suitable for use in the present invention are PolarTherm® 100 Series (PT 120, PT 140, PT 160 and
5 PT 180), 300 Series (PT 350) and 600 Series (PT 620, PT 630, PT 640 and PT 670) boron nitride powder particles which are commercially available from Advanced Ceramics Corporation of Lakewood, Ohio. "PolarTherm® Thermally Conductive Fillers for Polymeric Materials" a technical bulletin of Advanced Ceramics Corporation of Lakewood, Ohio (1996), which is hereby
10 incorporated by reference. These particles have a thermal conductivity of about 250-300 Watts per meter °K at 25°C, a dielectric constant of about 3.9 and a volume resistivity of about 10^{15} ohm-centimeters. The 100 Series powder has an average particle size ranging from about 5 to about 14 micrometers, the 300 Series has an average particle size ranging from about
15 100 to about 150 micrometers and the 600 series has an average particle size ranging from about 16 to greater than about 200 micrometers.

The solid lubricant particles 18 can be present in a dispersion, suspension or emulsion in water. Other solvents, such as mineral oil or alcohol (preferably less than about 5 weight percent), can be included in the
20 sizing composition, if desired. A non-limiting example of a preferred dispersion of about 25 weight percent boron nitride particles in water is ORPAC BORON NITRIDE RELEASECOAT-CONC which is commercially available from ZYP Coatings, Inc. of Oak Ridge, Tennessee. "ORPAC BORON NITRIDE RELEASECOAT-CONC", a technical bulletin of ZYP
25 Coatings, Inc., which is hereby incorporated by reference. According to the supplier, the boron nitride particles in this product have an average particle size of less than about 3 micrometers. This dispersion has about 1 percent of magnesium-aluminum silicate, which according to the supplier binds the boron nitride particles to the substrate to which the dispersion is applied.

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Other useful products which are commercially available from ZYP Coatings include BORON NITRIDE LUBRICOAT® paint, BRAZE STOP and WELD RELEASE products.

In an alternative embodiment, sizing, secondary coating or tertiary
5 coating compositions according to the present invention can include fillers containing soluble silicon-based groups which will react with alkali materials such as cement to form alkali-silicates which inhibit alkali attack of the glass surface. Preferably, the filler also contains a polyvalent metal cation such as aluminum. Example of such fillers include silane-treated calcium carbonate,
10 kaolin, silicas, aluminosilicates and pozzolanic materials such as fly ash.

In the preferred embodiment, the sizing composition is preferably essentially free of hydratable inorganic solid lubricant particles or abrasive silica particles or calcium carbonate, i.e., comprises less than about 20 weight percent of hydratable inorganic lubricant particles, abrasive silica
15 particles or calcium carbonate on a total solids basis, more preferably less than about 5 weight percent, and most preferably less than 0.001 weight percent.

As used herein, "hydratable" means that the solid inorganic lubricant particles react with molecules of water to form hydrates and contain water of
20 hydration or water of crystallization. A "hydrate" is produced by the reaction of molecules of water with a substance in which the H-OH bond is not split. See R. Lewis, Sr., Hawley's Condensed Chemical Dictionary, (12th Ed. 1993) at pages 609-610 and T. Perros, Chemistry, (1967) at pages 186-187, which are hereby incorporated by reference. In the chemical formulas of hydrates,
25 the addition of the water molecules is conventionally indicated by a centered dot, e.g., $3\text{MgO} \bullet 4\text{SiO}_2 \bullet \text{H}_2\text{O}$ (talc), $\text{Al}_2\text{O}_3 \bullet 2\text{SiO}_2 \bullet 2\text{H}_2\text{O}$ (kaolinite). Hydrates contain coordinated water, which coordinates the cations in the hydrated material and cannot be removed without the breakdown of the structure, and/or structural water, which occupies interstices in the structure to add to

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the electrostatic energy without upsetting the balance of charge. R. Evans, An Introduction to Crystal Chemistry, (1948) at page 276, which is hereby incorporated by reference.

While not preferred, the aqueous sizing composition can contain

5 hydratable or hydrated inorganic solid lubricant materials in addition to the non-hydratable inorganic solid lubricant materials discussed above. Non-limiting examples of such hydratable inorganic solid lubricant materials are clay mineral phyllosilicates, including micas (such as muscovite), talc, montmorillonite, kaolinite and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$).

10 In an alternative preferred embodiment, the inorganic solid particles 18 are thermally conductive, i.e., have a thermal conductivity greater than about 30 Watts per meter K, such as for example boron nitride, graphite, and the metallic inorganic solid lubricants discussed above. The thermal conductivity of a solid material can be determined by any method known to one skilled in

15 the art, such as the guarded hot plate method according to ASTM C-177-85 (which is hereby incorporated by reference) at a temperature of about 300K.

In another alternative preferred embodiment, the inorganic solid particles 18 are electrically insulative or have high electrical resistivity, i.e., have an electrical resistivity greater than about 1000 microhm-cm, such as

20 for example boron nitride.

The inorganic solid lubricant particles comprise greater than 20 to about 99 weight percent of the sizing composition on a total solids basis, preferably greater than 25 to about 80 weight percent, and more preferably greater than about 50 to about 60 weight percent.

25 In addition to the inorganic solid particles, the aqueous sizing composition preferably comprises one or more polymeric film-forming materials, such as thermosetting materials, thermoplastic materials, starches and mixtures thereof. Preferably the polymeric film-forming materials form a generally continuous film when applied to the surface 16 of the glass fibers.

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Generally, the amount of polymeric film-forming materials can range from about 1 to about 99 weight percent of the aqueous sizing composition on a total solids basis, preferably about 20 to about 75 weight percent and more preferably about 40 to about 50 weight percent.

- 5 Thermosetting polymeric film-forming materials are preferred polymeric film-forming materials for use in the aqueous sizing composition for coating glass fiber strands of the present invention. Such materials are compatible with thermosetting matrix materials used as laminates for printed circuit boards, such as FR-4 epoxy resins, which are polyfunctional epoxy resins
10 and in one particular embodiment of the invention is a difunctional brominated epoxy resins. See, 1 Electronic Materials HandbookTM, ASM International (1989) at pages 534-537, which are hereby incorporated by reference.

- Useful thermosetting materials include thermosetting polyesters, epoxy materials, vinyl esters, phenolics, aminoplasts, thermosetting polyurethanes
15 and mixtures thereof. Suitable thermosetting polyesters include STYPOL polyesters which are commercially available from Cook Composites and Polymers of Port Washington, Wisconsin and NEOXIL polyesters which are commercially available from DSM B.V. of Como, Italy.

- In a preferred embodiment, the thermosetting polymeric material is an
20 epoxy material. Useful epoxy materials contain at least one epoxy or oxirane group in the molecule, such as polyglycidyl ethers of polyhydric alcohols or thiols. Examples of suitable epoxy film-forming polymers include EPON® 826 and EPON® 880 epoxy resins, which are commercially available from Shell Chemical Company of Houston, Texas.

- 25 Useful thermoplastic polymeric materials include vinyl polymers, thermoplastic polyesters, polyolefins, polyamides (e.g. aliphatic polyamides or aromatic polyamides such as aramid), thermoplastic polyurethanes, acrylic polymers and mixtures thereof. Preferred vinyl polymers useful in the present invention include polyvinyl pyrrolidones such as PVP K-15, PVP K-30, PVP K-

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60 and PVP K-90, each of which are commercially available from ISP Chemicals of Wayne, New Jersey. Other suitable vinyl polymers include Resyn 2828 and Resyn 1037 vinyl acetate copolymer emulsions which are commercially available from National Starch, and other polyvinyl acetates
5 such as are commercially available from H. B. Fuller and Air Products and Chemicals Co. of Allentown, Pennsylvania.

Thermoplastic polyesters useful in the present invention include DESMOPHEN 2000 and DESMOPHEN 2001KS, both of which are commercially available from Bayer of Pittsburgh, Pennsylvania. A preferred
10 polyester is RD-847A polyester resin which is commercially available from Borden Chemicals of Columbus, Ohio. Useful polyamides include the VERSAMID products which are commercially available from General Mills Chemicals, Inc. Useful thermoplastic polyurethanes include WITCOBOND® W-290H which is commercially available from Witco Chemical Corp. of
15 Chicago, Illinois and RUCOTHANE® 2011L polyurethane latex which is commercially available from Ruco Polymer Corp. of Hicksville, New York.

The aqueous sizing composition can comprise a mixture of one or more thermosetting polymeric materials with one or more thermoplastic polymeric materials. In a preferred embodiment for laminates for printed
20 circuit boards, the polymeric materials of the aqueous sizing composition comprise a mixture of RD-847A polyester resin, PVP K-30 polyvinyl pyrrolidone, DESMOPHEN 2000 polyester and VERSAMID polyamide. In an alternative preferred embodiment suitable for laminates for printed circuit boards, the polymeric materials of the aqueous sizing composition comprise a
25 mixture of EPON 826 epoxy resin and PVP K-30 polyvinyl pyrrolidone.

Useful starches include those prepared from potatoes, corn, wheat, waxy maize, sago, rice, milo and mixtures thereof. A non-limiting example of a useful starch is Kollotex 1250 (a low viscosity, low amylose potato-based

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starch etherified with ethylene oxide) which is commercially available from AVEBE of the Netherlands.

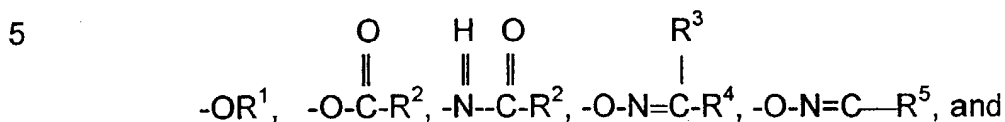
The polymeric materials can be water soluble, emulsifiable, dispersible and/or curable. As used herein, "water soluble" means that the polymeric
5 materials are capable of being essentially uniformly blended and/or molecularly or ionically dispersed in water to form a true solution. See Hawley's at page 1075, which is hereby incorporated by reference.

"Emulsifiable" means that the polymeric materials are capable of forming an essentially stable mixture or being suspended in water in the presence of an
10 emulsifying agent. See Hawley's at page 461, which is hereby incorporated by reference. Non-limiting examples of suitable emulsifying agents are set forth below. "Dispersible" means that any of the components of the polymeric materials are capable of being distributed throughout water as finely divided particles, such as a latex. See Hawley's at page 435, which is hereby
15 incorporated by reference. The uniformity of the dispersion can be increased by the addition of wetting, dispersing or emulsifying agents (surfactants), which are discussed below. "Curable" means that the polymeric materials and other components of the sizing composition are capable of being coalesced into a film or crosslinked to each other to change the physical
20 properties of the polymeric materials. See Hawley's at page 331, which is hereby incorporated by reference.

In addition to or in lieu of the polymeric materials discussed above, the aqueous sizing composition preferably comprises one or more glass fiber
coupling agents such as organo silane coupling agents, transition metal
25 coupling agents, phosphonate coupling agents, aluminum coupling agents, amino-containing Werner coupling agents and mixtures thereof. These coupling agents typically have dual functionality. Each metal or silicon atom has attached to it one or more groups which can react or compatibilize with the fiber surface and/or the components of the aqueous sizing composition.

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As used herein, the term "compatibilize" means that the groups are chemically attracted, but not bonded, to the fiber surface and/or the components of the sizing composition, for example by polar, wetting or solvation forces. Examples of hydrolyzable groups include:



the monohydroxy and/or cyclic C₂-C₃ residue of a 1,2- or 1,3 glycol, wherein

10 R¹ is C₁-C₃ alkyl; R² is H or C₁-C₄ alkyl; R³ and R⁴ are independently selected from H, C₁-C₄ alkyl or C₆-C₈ aryl; and R⁵ is C₄-C₇ alkylene. Examples of suitable compatibilizing or functional groups include epoxy, glycidoxy, mercapto, cyano, allyl, alkyl, urethano, halo, isocyanato, ureido, imidazoliny, vinyl, acrylato, methacrylato, amino or polyamino groups.

15 Functional organo silane coupling agents are preferred for use in the present invention. Examples of useful functional organo silane coupling agents include gamma-aminopropyltrialkoxysilanes, gamma-isocyanatopropyltriethoxysilane, vinyl-trialkoxysilanes, glycidoxypropyltrialkoxysilanes and ureidopropyltrialkoxysilanes. Preferred

20 functional organo silane coupling agents include A-187 gamma-glycidoxypropyltrimethoxysilane, A-174 gamma-methacryloxypropyltrimethoxysilane, A-1100 gamma-aminopropyltriethoxysilane silane coupling agents, A-1108 amino silane coupling agent and A-1160 gamma-ureidopropyltriethoxysilane (each of which are commercially available from OSi Specialties, Inc. of

25 Tarrytown, New York). The organo silane coupling agent can be at least partially hydrolyzed with water prior to application to the fibers, preferably at about a 1:1 stoichiometric ratio or, if desired, applied in unhydrolyzed form.

Suitable transition metal coupling agents include titanium, zirconium, yttrium and chromium coupling agents. Suitable titanate coupling agents and

30 zirconate coupling agents are commercially available from Kenrich Petrochemical Company. Suitable chromium complexes are commercially

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available from E.I. duPont de Nemours of Wilmington, Delaware. The amino-containing Werner-type coupling agents are complex compounds in which a trivalent nuclear atom such as chromium is coordinated with an organic acid having amino functionality. Other metal chelate and coordinate type coupling agents known to those skilled in the art can be used herein.

The amount of coupling agent can range from about 1 to about 99 weight percent of the aqueous sizing composition on a total solids basis, and preferably about 1 to about 10 weight percent.

The aqueous sizing composition can further comprise one or more organic lubricants which are chemically different from the polymeric materials discussed above. While the aqueous sizing composition can comprise up to about 60 weight percent organic lubricants, preferably the sizing composition is essentially free of organic lubricants, i.e., contains less than about 20 weight percent of organic lubricants, and more preferably is free of organic lubricants. Such organic lubricants include cationic, non-ionic or anionic lubricants and mixtures thereof, such as amine salts of fatty acids, alkyl imidazoline derivatives such as CATION X, which is commercially available from Rhone Poulenc of Princeton, New Jersey, acid solubilized fatty acid amides, condensates of a fatty acid and polyethylene imine and amide substituted polyethylene imines, such as EMERY® 6717, a partially amidated polyethylene imine commercially available from Henkel Corporation of Kankakee, Illinois.

The aqueous sizing composition can include one or more emulsifying agents for emulsifying or dispersing components of the aqueous sizing composition, such as the inorganic particles. Non-limiting examples of suitable emulsifying agents or surfactants include polyoxyalkylene block copolymers (such as PLURONIC™ F-108 polyoxypropylene-polyoxyethylene copolymer which is commercially available from BASF Corporation of Parsippany, New Jersey), ethoxylated alkyl phenols (such as IGEPAL CA-630

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ethoxylated octylphenoxyethanol which is commercially available from GAF Corporation of Wayne, New Jersey), polyoxyethylene octylphenyl glycol ethers, ethylene oxide derivatives of sorbitol esters, polyoxyethylated vegetable oils (such as ALKAMULS EL-719, which is commercially available
5 from Rhone-Poulenc) and nonylphenol surfactants (such as MACOL NP-6 which is commercially available from BASF of Parsippany, New Jersey). Generally, the amount of emulsifying agent can range from about 1 to about 30 weight percent of the aqueous sizing composition on a total solids basis.

The aqueous sizing composition can include one or more aqueous
10 soluble, emulsifiable or dispersible wax materials such as vegetable, animal, mineral, synthetic or petroleum waxes. Preferred waxes are petroleum waxes such as MICHEM® LUBE 296 microcrystalline wax, POLYMEKON® SPP-W microcrystalline wax and PETROLITE 75 microcrystalline wax which are commercially available from Michelman Inc. of Cincinnati, Ohio and the
15 Petrolite Corporation of Tulsa, Oklahoma, respectively. Generally, the amount of wax can be about 1 to about 10 weight percent of the sizing composition on a total solids basis.

Crosslinking materials, such as melamine formaldehyde, and plasticizers, such as phthalates, trimellitates and adipates, can also be
20 included in the aqueous sizing composition. The amount of crosslinker or plasticizer can range from about 1 to about 5 weight percent of the sizing composition on a total solids basis.

Other additives can be included in the aqueous sizing composition, such as silicones, fungicides, bactericides and anti-foaming materials,
25 generally in an amount of less than about 5 weight percent. Organic and/or inorganic acids or bases in an amount sufficient to provide the aqueous sizing composition with a pH of about 2 to about 10 can also be included in the sizing composition. A non-limiting example of a suitable silicone emulsion is LE-9300 epoxidized silicone emulsion which is commercially available from

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OSi Specialties, Inc. of Danbury, Connecticut. An example of a suitable bactericide is Biomet 66 antimicrobial compound, which is commercially available from M & T Chemicals of Rahway, New Jersey. Suitable anti-foaming materials are the SAG materials which are commercially available
5 from OSi Specialties, Inc. of Danbury, Connecticut and MAZU DF-136 which is available from BASF Company of Parsippany, New Jersey. Ammonium hydroxide can be added to the sizing composition for sizing stabilization, if desired. Water (preferably deionized) is included in the aqueous sizing composition in an amount sufficient to facilitate application of a generally
10 uniform coating upon the strand. The weight percentage of solids of the aqueous sizing composition generally ranges from about 1 to about 20 weight percent.

The aqueous sizing composition is preferably essentially free of glass materials. As used herein, "essentially free of glass materials" means that the
15 sizing composition comprises less than 20 volume percent of glass matrix materials for forming glass composites, preferably less than about 5 volume percent, and more preferably is free of glass materials. Examples of such glass matrix materials include black glass ceramic matrix materials or aluminosilicate matrix materials such as are well known to those skilled in the
20 art.

In a preferred embodiment for weaving fabric for laminated printed circuit boards, the glass fibers of the coated fiber strands of the present invention have applied thereto a primary layer of a dried residue of an aqueous sizing composition comprising PolarTherm® 160 boron nitride
25 powder and/or BORON NITRIDE RELEASECOAT dispersion, EPON 826 epoxy film-forming material, PVP K-30 polyvinyl pyrrolidone, A-187 epoxy-functional organo silane coupling agent, ALKAMULS EL-719 polyoxyethylated vegetable oil, IGEPAL CA-630 ethoxylated octylphenoxyethanol, KESSCO PEG 600 polyethylene glycol monolaurate ester which is commercially

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available from Stepan Company of Chicago, Illinois and EMERY® 6717 partially amidated polyethylene imine.

In a more preferred embodiment for weaving cloth, glass fibers of the coated fiber strands of the present invention have applied thereto a primary
5 layer of a dried residue of an aqueous sizing composition comprising PolarTherm® 160 boron nitride powder and/or BORON NITRIDE RELEASECOAT dispersion, RD-847A polyester, PVP K-30 polyvinyl pyrrolidone, DESMOPHEN 2000 polyester, A-174 acrylic-functional organo silane coupling agents and A-187 epoxy-functional organo silane coupling
10 agents, PLURONIC F-108 polyoxypropylene-polyoxyethylene copolymer, MACOL NP-6 nonylphenol surfactant, VERSAMID 140 and LE-9300 epoxidized silicone emulsion.

The aqueous sizing compositions of the present invention can be prepared by any suitable method such as conventional mixing well known to
15 those skilled in the art. Preferably, the components discussed above are diluted with water to have the desired weight percent solids and mixed together. Powdered solid particles can be premixed with water or added to the polymeric material prior to mixing with the other components of the sizing.

The primary layer of sizing can be applied in many ways, for example
20 by contacting the filaments with a roller or belt applicator, spraying or other means. The sized fibers are preferably dried at room temperature or at elevated temperatures. The dryer removes excess moisture from the fibers and, if present, cures any curable sizing composition components. The temperature and time for drying the glass fibers will depend upon such
25 variables as the percentage of solids in the sizing composition, components of the sizing composition and type of glass fiber. The sizing composition is typically present as a dried residue on the fibers in an amount between about 0.1 percent and about 5 percent by weight after drying.

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The fibers are gathered into strands having 1 to about 15,000 fibers per strand, and preferably about 100 to about 1600 fibers per strand. The average filament diameter of the fibers can range from about 3 to about 30 micrometers.

- 5 A secondary layer of a secondary coating composition can be applied over the primary layer in an amount effective to coat or impregnate the portion of the strands, for example by dipping the strand in a bath containing the composition, spraying the composition upon the strand or by contacting the strand with an applicator as discussed above. The coated strand can be
- 10 passed through a die to remove excess coating composition from the strand and/or dried as discussed above for a time sufficient to at least partially dry or cure the secondary coating composition. The method and apparatus for applying the secondary coating composition to the strand is determined in part by the configuration of the strand material. The strand is preferably dried
- 15 after application of the secondary coating composition in a manner well known in the art.

- Suitable secondary coating compositions can include one or more film-forming materials, lubricants and other additives such as are discussed above. The secondary coating is different from the sizing composition, i.e., it
- 20 (1) contains at least one component which is chemically different from the components of the sizing composition; or (2) contains at least one component in an amount which is different from the amount of the same component contained in the sizing composition. Non-limiting examples of suitable secondary coating compositions including polyurethane are disclosed in U.S.
- 25 Patent Nos. 4,762,750 and 4,762,751, which are hereby incorporated by reference.

Referring now to Fig. 2, in an alternative preferred embodiment according to the present invention, the glass fibers 212 of the coated fiber strand 210 can having applied thereto a primary layer 214 of a dried residue

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of a sizing composition which can include any of the sizing components in the amounts discussed above. Examples of suitable sizing compositions are set forth in Loewenstein at pages 237-291 (3d Ed. 1993) and U.S. Patent Nos. 4,390,647 and 4,795,678, each of which is hereby incorporated by reference.

- 5 A secondary or principal layer 215 of an aqueous secondary coating composition is applied to at least a portion, and preferably over the entire outer surface, of the primary layer 214. The aqueous secondary coating composition comprises one or more types of solid particles 216 such as are discussed in detail above. Preferably, the solid particles in the secondary
- 10 coating composition are non-hydratable, lamellar inorganic lubricant particles such as boron nitride which are discussed above. The amount of inorganic lubricant particles in the secondary coating composition can range from greater than 20 to about 99 weight percent on a total solids basis, preferably greater than 25 to about 80 weight percent, and more preferably greater than
- 15 50 to about 60 weight percent. The percentage of solids of the aqueous secondary coating composition generally ranges from about 5 to about 50 weight percent of the total weight of the sizing composition.

In an alternative embodiment, the solid particles of the secondary coating composition comprise hydrophilic inorganic solid particles which

20 absorb and retain water in the interstices of the hydrophilic particles. The hydrophilic inorganic solid particles can absorb water or swell when in contact with water or participate in a chemical reaction with the water to form, for example, a viscous gel-like solution which blocks or inhibits further ingress of water into the interstices of a telecommunications cable which the coated

25 glass fiber strand is used to reinforce. As used herein, "absorb" means that the water penetrates the inner structure or interstices of the hydrophilic material and is substantially retained therein. See Hawley's Condensed Chemical Dictionary at page 3, which is hereby incorporated by reference. "Swell" means that the hydrophilic particles expand in size or volume. See

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Webster's New Collegiate Dictionary (1977) at page 1178, which is hereby incorporated by reference. Preferably, the hydrophilic particles swell after contact with water to at least one and one-half times their original dry weight, and more preferably about two to about six times their original weight. Non-
5 limiting examples of hydrophilic inorganic solid lubricant particles which swell include smectites such as vermiculite and montmorillonite, absorbent zeolites and inorganic absorbent gels. Preferably, these hydrophilic particles are applied in powder form over tacky sizing or other tacky secondary coating materials. The amount of hydrophilic inorganic particles in this embodiment
10 of the secondary coating composition can range from about 1 to about 99 weight percent on a total solids basis, preferably greater than 20 to about 99 weight percent on a total solids basis, more preferably greater than 25 to about 80 weight percent, and even more preferably greater than 50 to about 60 weight percent.

15 In an alternative embodiment shown in Fig. 3, a tertiary layer 320 of a tertiary coating composition can be applied to at least a portion of the surface, and preferably over the entire surface, of a secondary layer 315 of coated fiber strand 310, i.e., such a fiber strand 312 would have a primary layer 314 of sizing, a secondary layer 315 of a secondary coating composition and a
20 tertiary, outer layer 320 of the tertiary coating. The tertiary coating is different from the sizing composition and the secondary coating composition, i.e., the tertiary coating composition (1) contains at least one component which is chemically different from the components of the sizing and secondary coating composition; or (2) contains at least one component in an amount which is
25 different from the amount of the same component contained in the sizing or secondary coating composition.

In this embodiment, the secondary coating composition comprises one or more polymeric materials discussed above, such as polyurethane, and the tertiary powdered coating composition comprises powdered solid particles,

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such as the PolarTherm® boron nitride particles which are discussed above. Preferably, the powdered coating is applied by passing the strand having a liquid secondary coating composition applied thereto through a fluidized bed or spray device to adhere the powder particles to the tacky secondary coating composition. Alternatively, the strands can be assembled into a fabric 810 before the layer 812 of tertiary coating is applied, as shown in Fig. 8. The weight percent of powdered solid particles adhered to the coated fiber strand 310 can range from about 0.1 to about 30 weight percent of the total weight of the dried strand.

10 The tertiary powdered coating can also include one or more polymeric materials such as are discussed above, such as acrylic polymers, epoxies, or polyolefins, conventional stabilizers and other modifiers known in the art of such coatings, preferably in dry powder form.

15 The coated fiber strands 10, 210, 310 discussed above can be used as continuous strand or further processed into diverse products such as chopped strand, twisted strand, roving and/or fabric, such as wovens, non-wovens, knits and mats.

20 The coated fiber strands 10, 210, 310 and products formed therefrom can be used in a wide variety of applications, but are preferably used as reinforcements 410 for reinforcing polymeric matrix materials 412 to form a composite 414, such as is shown in Fig. 4, which will be discussed in detail below. Such applications include but are not limited to laminates for printed circuit boards, reinforcements for telecommunications cables, and various other composites. An advantage of the impregnated strands of the present invention is that the solid particles provide interstices between the fibers of the strand which facilitate flow of the matrix materials therebetween to more quickly and/or uniformly wet-out and wet-through the fibers of the strand. Surprisingly, the amount of solid particles can exceed 20 weight percent of the total solids of the coating composition applied to the fibers, yet still be

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adequately adhered to the fibers and provide strands having handling characteristics at least comparable to strands without the solid particle coating. Such inorganic particles are often less costly than conventional glass fiber coating components and, when used as an inorganic filler, can
5 reduce fiber production cost while maintaining processability and composite physical properties.

In a preferred embodiment shown in Fig. 5, the coated fiber strands 510 made according to the present invention can be used as warp and/or weft strands 514, 516 in a knit or woven fabric 512 reinforcement, preferably
10 to form a laminate for a printed circuit board (shown in Figs. 6-8). The warp strands 514 can be twisted prior to secondary coating by any conventional twisting technique known to those skilled in the art, for example by using twist frames to impart twist to the strand at about 0.5 to about 3 turns per inch. The reinforcing fabric 512 can include about 5 to about 50 warp strands 514
15 and preferably has about 3 to about 25 picks per centimeter (about 1 to about 15 picks per inch) of the weft strand 516. A suitable woven reinforcing fabric 512 can be formed by using any conventional loom well known to those skilled in the art, such as a shuttle loom, air jet loom or rapier loom. A preferred loom is a Tsudakoma loom which is commercially available from
20 Tsudakoma of Japan. The weave construction can be a regular plain weave or mesh (shown in Fig. 5), although any other weaving style well known to those skilled in the art, such as a twill weave or satin weave, can be used.

Referring now to Fig. 6, the fabric 612 can be used to form a composite or laminate 614 by coating and/or impregnating with a polymeric
25 film-forming thermoplastic or thermosetting matrix material 616. The composite or laminate 614 is suitable for use as an electronic support. As used herein, "electronic support" means a structure that mechanically supports and/or electrically interconnects elements including but not limited to active electronic components, passive electronic components, printed circuits,

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integrated circuits, semiconductor devices and other hardware associated with such elements including but not limited to connectors, sockets, retaining clips and heat sinks.

Matrix materials useful in the present invention include thermosetting materials such as thermosetting polyesters, vinyl esters, epoxides (containing at least one epoxy or oxirane group in the molecule, such as polyglycidyl ethers of polyhydric alcohols or thiols), phenolics, aminoplasts, thermosetting polyurethanes, derivatives and mixtures thereof. Preferred matrix materials for forming laminates for printed circuit boards are FR-4 epoxy resins, polyimides and liquid crystalline polymers, the compositions of which are well known to those skilled in the art. If further information regarding such compositions is needed, see 1 Electronic Materials Handbook™, ASM International (1989) at pages 534-537.

Non-limiting examples of suitable polymeric thermoplastic matrix materials include polyolefins, polyamides, thermoplastic polyurethanes and thermoplastic polyesters, vinyl polymers and mixtures thereof. Further examples of useful thermoplastic materials include polyimides, polyether sulfones, polyphenyl sulfones, polyetherketones, polyphenylene oxides, polyphenylene sulfides, polyacetals, polyvinyl chlorides and polycarbonates.

Other components which can be included with the polymeric matrix material and reinforcing material in the composite include colorants or pigments, lubricants or processing aids, ultraviolet light (UV) stabilizers, antioxidants, other fillers and extenders.

The fabric 612 can be coated and impregnated by dipping the fabric 612 in a bath of the polymeric matrix material 616, for example, as discussed in R. Tummala (Ed.), Microelectronics Packaging Handbook, (1989) at pages 895-896, which are hereby incorporated by reference. More generally, chopped or continuous fiber strand reinforcing material can be dispersed in the matrix material by hand or any suitable automated feed or mixing device

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which distributes the reinforcing material generally evenly throughout the polymeric matrix material. For example, the reinforcing material can be dispersed in the polymeric matrix material by dry blending all of the components concurrently or sequentially.

- 5 The polymeric matrix material 616 and strand can be formed into a composite or laminate 614 by a variety of methods which are dependent upon such factors as the type of polymeric matrix material used. For example, for a thermosetting matrix material, the composite can be formed by compression or injection molding, pultrusion, filament winding, hand lay-up, spray-up or by
- 10 sheet molding or bulk molding followed by compression or injection molding. Thermosetting polymeric matrix materials can be cured by the inclusion of crosslinkers in the matrix material and/or by the application of heat, for example. Suitable crosslinkers useful to crosslink the polymeric matrix material are discussed above. The temperature and curing time for the
- 15 thermosetting polymeric matrix material depends upon such factors as the type of polymeric matrix material used, other additives in the matrix system and thickness of the composite, to name a few.

For a thermoplastic matrix material, suitable methods for forming the composite include direct molding or extrusion compounding followed by

20 injection molding. Methods and apparatus for forming the composite by the above methods are discussed in I. Rubin, Handbook of Plastic Materials and Technology (1990) at pages 955-1062, 1179-1215 and 1225-1271, which are hereby incorporated by reference.

In a particular embodiment of the invention shown in Fig. 7, composite

25 or laminate 710 includes fabric 712 impregnated with a compatible matrix material 714. The impregnated fabric can then be squeezed between a set of metering rolls to leave a measured amount of matrix material, and dried to form an electronic support in the form of a semicured substrate or prepreg. An electrically conductive layer 720 can be positioned along a portion of a

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side 722 of the prepreg in a manner to be discussed below in the specification, and the prepreg is cured to form an electronic support 718 with an electrically conductive layer. In another embodiment of the invention, and more typically in the electronic support industry, two or more prepregs are
5 combined with an electrically conductive layer and laminated together and cured in a manner well known to those skilled in the art, to form a multilayered electronic support. For example, but not limiting the present invention, the prepreg stack can be laminated by pressing the stack, e.g. between polished steel plates, at elevated temperatures and pressures for a predetermined
10 length of time to cure the polymeric matrix and form a laminate of a desired thickness. A portion of one or more of the prepregs can be provided with an electrically conductive layer either prior to or after lamination and curing such that the resulting electronic support is a laminate having at least one electrically conductive layer along a portion of an exposed surface
15 (hereinafter referred to as a "clad laminate").

Circuits can then be formed from the electrically conductive layer(s) of the single layer or multilayered electronic support using techniques well known in the art to construct an electronic support in the form of a printed circuit board or printed wiring board (hereinafter collectively referred to as
20 "electronic circuit boards"). If desired, apertures or holes (also referred to as "vias") can be formed in the electronic supports, to allow for electrical interconnection between circuits and/or components on opposing surfaces of the electronic support, by any convenient manner known in the art, including but not limited to mechanical drilling and laser drilling. More specifically, after
25 formation of the apertures, a layer of electrically conductive material is deposited on the walls of the aperture or the aperture is filled with an electrically conductive material to facilitate the required electrical interconnection and/or heat dissipation.

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The electrically conductive layer 720 can be formed by any method well known to those skilled in the art. For example but not limiting the present invention, the electrically conductive layer can be formed by laminating a thin sheet or foil of metallic material onto at least a portion of a side of the semi-cured or cured prepreg or laminate. As an alternative, the electrically conductive layer can be formed by depositing a layer of metallic material onto at least a portion of a side of the semi-cured or cured prepreg or laminate using well known techniques including but not limited to electrolytic plating, electroless plating or sputtering. Metallic materials suitable for use as an electrically conductive layer include but are not limited to copper (which is preferred), silver, aluminum, gold, tin, tin-lead alloys, palladium and combinations thereof.

In another embodiment of the present invention, the electronic support can be in the form of a multilayered electronic circuit board constructed by laminating together one or more electronic circuit boards (described above) with one or more clad laminates (described above) and/or one or more prepreps (described above). If desired, additional electrically conductive layers can be incorporated into the electronic support, for example along a portion of an exposed side of the multilayered electronic circuit board.

Furthermore, if required, additional circuits can be formed from the electrically conductive layers in a manner discussed above. It should be appreciated that depending on the relative positions of the layers of the multilayered electronic circuit board, the board can have both internal and external circuits. Additional apertures are formed, as discussed earlier, partially through or completely through the board to allow electrical interconnection between the layers at selected locations. It should be appreciated that the resulting structure can have some apertures that extend completely through the structure, some apertures that extend only partially through the structure, and some apertures that are completely within the structure.

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The instant invention further contemplates the fabrication of multilayered laminates and electronic circuit boards which include at least one composite layer made according to the teachings herein and at least one composite layer made in a manner different from the composite layer taught herein, e.g. made using conventional glass fiber composite technology. More specifically and as is well known to those skilled in the art, traditionally the filaments in continuous glass fiber strands used in weaving fabric are treated with a starch/oil sizing which includes partially or fully dextrinized starch or amylose, hydrogenated vegetable oil, a cationic wetting agent, emulsifying agent and water, including but not limited to those disclosed in Loewenstein at pages 237-244 (3d Ed. 1993), which is hereby incorporated by reference. Warp yarns produced from these strands are thereafter treated with a solution prior to weaving to protect the strands against abrasion during the weaving process, e.g. poly(vinyl alcohol) as disclosed in U.S. Patent No. 4,530,876 at column 3, line 67 through column 4, line 11, which is hereby incorporated by reference. This operation is commonly referred to as slashing. The poly(vinyl alcohol) as well as the starch/oil size are generally not compatible with the polymeric matrix material used by composite manufacturers and the fabric must be cleaned to remove essentially all organic material from the surface of the glass fibers prior to impregnating the woven fabric. This can be accomplished in a variety ways, for example by scrubbing the fabric or, more commonly, by heat treating the fabric in a manner well known in the art. As a result of the cleaning operation, there is no suitable interface between the polymeric matrix material used to impregnate the fabric and the cleaned glass fiber surface, so that a coupling agent must be applied to the glass fiber surface. This operation is sometime referred to by those skilled in the art as finishing. The coupling agents most commonly used in finishing operations are silanes, including but not limited to those disclosed in E. P. Plueddemann, Silane Coupling Agents (1982) at pages 146-147, which is hereby

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incorporated by reference. Also see Lowenstein at pages 249-256 (3d Ed. 1993). After treatment with the silane, the fabric is impregnated with a compatible polymeric matrix material, squeezed between a set of metering rolls and dried to form a semicured prepreg as discussed above. It should be appreciated that depending on the nature of the sizing, the cleaning operation and/or the matrix resin used in the composite, the slashing and/or finishing steps can be eliminated. One or more prepregs incorporating conventional glass fiber composite technology can then be combined with one or more prepregs incorporating the instant invention to form an electronic support as discussed above, and in particular a multilayered laminate or electronic circuit board. For more information regarding fabrication of electronic circuit boards, see 1 Electronic Materials HandbookTM, ASM International (1989) at pages 113-115, R. Tummala (Ed.), Microelectronics Packaging Handbook, (1989) at pages 858-861 and 895-909, M. W. Jawitz, Printed Circuit Board Handbook (1997) at pages 9.1-9.42, and C. F. Coombs, Jr. (Ed.), Printed Circuits Handbook, (3d Ed. 1988), pages 6.1-6.7, which are hereby incorporated by reference.

The composites and laminates forming the electronic supports of the instant invention can be used to form packaging used in the electronics industry, and more particularly first, second and/or third level packaging, such as that disclosed in Tummala at pages 25-43, which is hereby incorporated by reference. In addition, the present invention can also be used for other packaging levels.

The present invention also includes a method for reinforcing a polymeric matrix material to form a composite. The method comprises:

- (1) applying to a glass fiber strand reinforcing material the above sizing, secondary coating and/or tertiary coating composition including greater than 20 weight percent on a total solids basis of inorganic solid particles; (2) drying the coating to form a substantially uniform coating upon the reinforcing

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material; (3) combining the reinforcing material with the polymeric matrix material; and (4) at least partially curing the polymeric matrix material to provide a reinforced polymeric composite in a manner such as is discussed in detail above. Although not limiting the present invention, the reinforcing

5 material can be combined with the polymeric matrix material, for example by dispersing it in the matrix material.

The present invention also includes a method for inhibiting adhesion between adjacent glass fibers of a glass fiber strand, comprising the steps of: (1) applying to a glass fiber strand the above sizing, secondary coating and/or

10 tertiary coating composition including greater than 20 weight percent on a total solids basis of inorganic solid particles which have a Mohs' hardness which is less than a Mohs' hardness of the glass fiber; (2) drying the coating to form a substantially uniform coating upon the glass fibers of the glass fiber strand, such that adhesion between adjacent glass fibers of the strand is

15 inhibited.

The present invention also includes a method for inhibiting hydrolysis of a polymeric matrix material of a glass fiber-reinforced composite. The method comprises: (1) applying to a glass fiber strand reinforcing material the above sizing, secondary coating and/or tertiary coating composition

20 including greater than 20 weight percent on a total solids basis of inorganic solid particles; (2) drying the coating to form a substantially uniform coating upon the reinforcing material; (3) combining the reinforcing material with the polymeric matrix material; and (4) at least partially curing the polymeric matrix material to provide a reinforced polymeric composite in a manner such as is

25 discussed in detail above. As discussed above, the reinforcing material can be combined with the polymeric matrix material, for example by dispersing it in the matrix material.

The present invention will now be illustrated by the following specific, non-limiting examples.

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EXAMPLE 1

Each of the components in the amounts set forth in Table 1 were mixed to form aqueous forming size compositions K through N according to
5 the present invention. Each aqueous forming size composition was prepared in a similar manner to that discussed above. Less than about 1 weight percent of acetic acid on a total weight basis was included in each composition.

Each of the aqueous forming size compositions of Table 1 was coated
10 onto 2G-18 E-glass fiber strands. Each of the forming size compositions had about 10 weight percent solids.

Table 1

COMPONENT	WEIGHT PERCENT OF COMPONENT ON TOTAL SOLIDS BASIS				
	Sample No.				
	K	L	M	N	Comparative Sample
Thermoplastic polyurethane film-forming polymer ²⁰	34.4	34.2	33.4	31.35	34.5
Thermoplastic polyurethane film-forming polymer ²¹	51.5	51.2	50.18	46.9	51.7
polyoxyalkylene polyol copolymer	0.3	0.3	0.3	0.3	0.33
epoxidized polyester lubricant	7.2	7.1	7.0	6.55	7.22
Gamma-aminopropyl triethoxysilane coupling agent	2.7	2.7	2.7	2.5	2.76
Gamma-ureidopropyl triethoxysilane coupling agent	3.3	3.3	3.2	3.0	3.34
amino-functional organo silane coupling agent	0.1	0.1	0.1	0.1	0.14
Boron nitride particles in aqueous suspension ²²	0.1	1.0	2.9	9.1	0
loss on ignition (%)	1.11	1.14	1.05	1.08	1.17

Composite samples of each of the above coated glass fiber samples and the Comparative Sample were extrusion molded at 270°C for 48 seconds at about 7 MPa (975 psi) to produce 254 x 254 x 3.175 millimeters (10 x 10 x 0.125 inches) plaques. Each specimen was evaluated for: tensile strength, tensile elongation and tensile modulus according to ASTM Method D-638M; flexural strength and flexural modulus according to ASTM Method D-790; and notched and unnotched Izod impact strength according to ASTM Method D-256 at the glass contents specified below.

Table 2 presents the results of tests conducted on composites formed using a conventional nylon 6,6 matrix resin.

²⁰ Thermoplastic polyester-based polyurethane aqueous emulsion having 65 percent solids, anionic particle charge, particle size of about 2 micrometers, a pH of 7.5 and a viscosity of 400 centipoise (Brookfield LVF) at 25°C.

²¹ Thermoplastic polyester-based polyurethane aqueous dispersion having a solids content of 62 percent, pH of about 10 and average particle size ranging from about 0.8 to about 2.5 microns.

²² ORPAC BORON NITRIDE RELEASECOAT-CONC boron nitride particles in aqueous dispersion which is commercially available from ZYP Coatings, Inc. of Oak Ridge, Tennessee.

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TABLE 2

	units	K	L	M	N	Comp. Sample
Tensile Strength	kpsi	27.1	27.6	27.3	27.4	26.2
	MPa	186.9	190.34	188.27	188.96	180.68
Tensile Elongation	%	3.32	3.37	3.36	3.42	3.32
Tensile Modulus	mpsi	1.48	1.55	1.47	1.44	1.51
	GPa	10.2	10.7	10.1	9.9	10.4
Flexural Strength	kpsi	44.6	46.3	45.7	45.5	44.0
	MPa	307.6	319.3	315.2	313.8	303.4
Flexural Modulus	mpsi	1.52	1.56	1.54	1.54	1.5
	GPa	10.5	10.7	10.6	10.6	10.6
notched IZOD Impact	ft lb _f /in	1.86	2.24	1.94	1.63	1.16
	kJ/m ²	7.89	9.50	8.23	6.91	4.92
unnotched IZOD Impact	ft lb _f /in	21.8	22.9	21.1	20.5	22.0
	kJ/m ²	92.43	97.10	89.46	86.92	93.28
Glass content	%	32.9	32.6	32.4	32.3	32.4

- As shown in Table 2, glass fiber strands coated with boron nitride
- 5 particles (Samples K-N) according to the present invention exhibit improved tensile strength and notched Izod impact properties and similar tensile elongation and modulus, flexural strength and modulus and unnotched Izod impact properties when compared to a comparative sample having similar components which did not contain boron nitride in nylon 6,6 reinforcement.
- 10 When evaluated using nylon 6 resin under similar conditions, the improvements in tensile strength and notched Izod impact properties were not observed.

EXAMPLE 2

- 15 Each of the components in the amounts set forth in Table 3 were mixed to form aqueous forming size compositions P through S according to the present invention. Each aqueous forming size composition was prepared in a similar manner to that discussed above. Less than about 1 weight

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percent of acetic acid on a total weight basis was included in each composition.

Each of the aqueous forming size compositions of Table 3 was coated onto G-31 E-glass fiber strands. Each of the forming size compositions had about 10 weight percent solids.

Table 3

COMPONENT	WEIGHT PERCENT OF COMPONENT ON TOTAL SOLIDS BASIS			
	Sample No.			
	P	Q	R	S
Thermoplastic polyurethane film-forming polymer ²³	23	28.75	28.75	23
Thermoplastic polyurethane film-forming polymer ²⁴	34.45	43.1	43.1	34.45
polyoxyalkylene polyol copolymer	0.22	0.27	0.27	0.22
epoxidized polyester lubricant	4.8	6.0	6.0	4.8
Gamma-aminopropyl triethoxysilane coupling agent	1.84	2.3	2.3	1.84
Gamma-ureidopropyl triethoxysilane coupling agent	2.22	2.78	2.78	2.22
amino-functional organo silane coupling agent	0.1	0.12	0.12	0.1
Boron nitride powder particles ²⁵	33.3	16.7	0	0
talc powder particles ²⁶	0	0	16.7	33.3
loss on ignition (%)	0.52	0.81	0.80	0.64

Composite samples of each of the above coated glass fiber samples and the Comparative Sample of Table 1 above were extrusion molded to produce 400 x 400 x 2.5 millimeters (16 x 16 x 0.100 inches) plaques under

²³ Thermoplastic polyester-based polyurethane aqueous emulsion having 65 percent solids, anionic particle charge, particle size of about 2 micrometers, a pH of 7.5 and a viscosity of 400 centipoise (Brookfield LVF) at 25°C.

²⁴ Thermoplastic polyester-based polyurethane aqueous dispersion having a solids content of 62 percent, pH of about 10 and average particle size ranging from about 0.8 to about 2.5 microns.

²⁵ PolarTherm® PT 160 boron nitride powder particles which are commercially available from Advanced Ceramics Corporation of Lakewood, Ohio.

²⁶ VANTALC 2003 talc powder particles which are commercially available from R.T. Vanderbilt Company, Inc. of Norwalk, Connecticut.

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the conditions set forth in Example 1 above. Each specimen was evaluated for: tensile strength, tensile elongation, tensile modulus, notched and unnotched Izod impact strength as discussed in Example 1 above at the glass contents specified below.

- 5 The color tests were performed on composites having a thickness of 3.175 millimeters (1/8 inch) and a diameter of 76.2 millimeters (3 inches) using a Hunter colorimeter Model D25-PC2A. To evaluate material handling characteristics, funnel flow tests were conducted on samples of chopped glass fiber. The funnel was eighteen inches long and had a seventeen inch
10 diameter opening at the top and a two inch opening on the bottom. The funnel was vibrated and the time was recorded for 20 pounds of sample material to flow through the funnel. The PD-104 test evaluates the resistance of the chopped glass fiber sample to filamentation. Sixty grams of sample, 140 grams of an abrasive material (ground walnut shell particles No. 6/10
15 which are commercially available from Hammon Products Company) and a conventional foam type antistatic dryer sheet were enclosed in a 4 liter stainless steel beaker and vibrated using a Red Devil paint shaker Model 5400E3 for six minutes. The vibrated material was screened using No. 5 and No. 6 U.S. Standard testing sieves. The weight percent of fuzz material
20 collected on the screens as a percentage of original sample is reported below.

Table 4 presents the results of tests conducted on composites formed using Samples P-S and the Comparative Sample using nylon 6,6 matrix resin.

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TABLE 4

	units	P	Q	R	S	Comp. Sample
Tensile Strength	kpsi	29.5	28.6	28.7	27.7	29.6
	MPa	203.5	197.2	197.9	191.0	204.1
Tensile Elongation	%	3.03	3.05	2.98	2.97	3.01
Tensile Modulus	kpsi	1866	1779	1720	1741	1748
	GPa	12.86	12.26	11.86	12.0	12.05
notched IZOD Impact	ft lb _f /in	2.10	1.96	1.94	1.78	2.26
	kJ/m ²	8.90	8.31	8.23	7.55	9.58
unnotched IZOD Impact	ft lb _f /in	24.9	23.4	22.8	22.2	26.4
	kJ/m ²	105.58	99.22	96.67	94.13	111.94
Actual Loss on Ignition	%	0.81	0.52	0.80	0.64	1.17
PD 104	%	1.3	0.7	0.1	1.4	0.1
Funnel Flow	seconds	13.8	15.2	15.4	23.5	13.0
Whiteness Index		-15.1	-12.0	-17.6	-18.5	-18.2
Yellowness Index		40.0	37.5	42.5	43.4	43.6
Glass content	%	33.30	33	32.90	31.70	33.80

As shown in Table 4, glass fiber strands coated with boron nitride particles (Samples P-S) according to the present invention exhibit improved

5 whiteness and yellowness and similar tensile strength, elongation and modulus, flexural strength and modulus, and notched and unnotched Izod impact properties when compared to a Comparative Sample having similar components which did not contain boron nitride in nylon 6,6 reinforcement.

10

EXAMPLE 3

Each of the components in the amounts set forth in Table 5 were mixed to form aqueous forming size compositions T and U according to the present invention. Each aqueous forming size composition was prepared in a similar manner to that discussed above. Less than about 1 weight percent of

15 acetic acid on a total weight basis was included in each composition. Table 5 presents the results of whiteness and yellowness tests conducted on composites formed using Samples T, U and the Comparative Sample using nylon 6,6 matrix resin. The color tests were performed on composites having

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a thickness of 3.175 millimeters (1/8 inch) and a diameter of 76.2 millimeters (3 inches) using a Hunter colorimeter Model D25-PC2A.

Table 5

COMPONENT	WEIGHT PERCENT OF COMPONENT ON TOTAL SOLIDS BASIS		
	Sample No.		
	T	U	Comparative Sample
Thermoplastic polyurethane film-forming polymer ²⁷	31.35	28.75	34.4
Thermoplastic polyurethane film-forming polymer ²⁸	46.9	43.1	51.6
polyoxyalkylene polyol copolymer	0.3	0.27	0.3
epoxidized polyester lubricant	6.55	6.0	7.2
Gamma-aminopropyl triethoxysilane coupling agent	2.5	2.3	2.7
Gamma-ureidopropyl triethoxysilane coupling agent	3.0	2.78	3.3
amino-functional organo silane coupling agent	0.1	0.12	0.1
Boron nitride particles in aqueous suspension ²⁹	9.1	16.7	0
Whiteness Index	-16.3	-15.0	-20.7
Yellowness Index	39.3	38.1	42.7

5

As is shown in Table 5, Samples T and U, each coated with a sizing composition containing boron nitride particles according to the present invention, had lower whiteness indices in nylon 6,6 than a Comparative Sample of a similar formulation which did not include boron nitride.

10

EXAMPLE 4

The components in the amounts set forth in Table 6 were mixed to form aqueous forming size compositions A-D according to the present

²⁷ Thermoplastic polyester-based polyurethane aqueous emulsion having 65 percent solids, anionic particle charge, particle size of about 2 micrometers, a pH of 7.5 and a viscosity of 400 centipoise (Brookfield LVF) at 25°C.

²⁸ Thermoplastic polyester-based polyurethane aqueous dispersion having a solids content of 62 percent, pH of about 10 and average particle size ranging from about 0.8 to about 2.5 microns.

²⁹ ORPAC BORON NITRIDE RELEASECOAT-CONC boron nitride particles in aqueous dispersion which is commercially available from ZYP Coatings, Inc. of Oak Ridge, Tennessee.

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invention in a similar manner to that discussed above. Less than 1 weight percent of acetic acid was included in each composition.

Table 6

COMPONENT	WEIGHT PERCENT OF COMPONENT ON TOTAL SOLIDS BASIS				
	SAMPLE NO.				
	A	B	C	D	Comp. Sample No. 1
Thermoplastic polyester film-forming polymer ³⁰	28.6	29.1	31.58	50.71	28.9
Thermoplastic polyester film-forming polymer ³¹	43.7	39.1	0	0	44.1
Epoxy film-forming polymer ³²	0	0	21.05	0	0
Polyvinyl pyrrolidone ³³	0	9.7	15.79	15.21	0
epoxy-functional organo silane coupling agent ³⁴	2.3	2.3	8.42	8.11	2.3
acrylic-functional organo silane coupling agent ³⁵	4.7	4.8	0	0	4.8
amino-functional organo silane coupling agent ³⁶	0	0	8.42	8.11	0
polyoxyalkylene block copolymer ³⁷	10.7	5.6	0	0	10.9
Ethoxylated octylphenoxyethanol ³⁸	0	0	4.74	6.39	0
polyamide ³⁹	4.8	4.8	0	0	4.8
surfactant ⁴⁰	3.6	3.6	4.74	6.39	3.6
Organic lubricant ⁴¹	0	0	4.21	4.06	0
polyoxyethylene polymer ⁴²	0.6	0	0	0	0.6
boron nitride powder particles ⁴³	1.0	1.0	0	0	0
boron nitride particles in aqueous suspension ⁴⁴	0	0	1.05	1.01	0

³⁰ RD-847A polyester resin which is commercially available from Borden Chemicals of Columbus, Ohio.

³¹ DESMOPHEN 2000 polyethylene adipate diol which is commercially available from Bayer of Pittsburgh, Pennsylvania.

³² EPI-REZ® 3522-W-66 which is commercially available from Shell Chemical Co. of Houston, Texas.

³³ PVP K-30 polyvinyl pyrrolidone which is commercially available from ISP Chemicals of Wayne, New Jersey.

³⁴ A-187 gamma-glycidoxypolytrimethoxysilane which is commercially available from OSi Specialties, Inc. of Tarrytown, New York.

³⁵ A-174 gamma-methacryloxypropyltrimethoxysilane which is commercially available from OSi Specialties, Inc. of Tarrytown, New York.

³⁶ A-1100 amino-functional organo silane coupling agent which is commercially available from OSi Specialties, Inc. of Tarrytown, New York.

³⁷ PLURONIC™ F-108 polyoxypropylene-polyoxyethylene copolymer which is commercially available from BASF Corporation of Parsippany, New Jersey.

³⁸ IGEPAL CA-630 ethoxylated octylphenoxyethanol which is commercially available from GAF Corporation of Wayne, New Jersey.

³⁹ VERSAMID 140 polyamide which is commercially available from General Mills Chemicals, Inc.

⁴⁰ MACOL NP-6 nonylphenol surfactant which is commercially available from BASF of Parsippany, New Jersey.

⁴¹ EMERY® 6760 lubricant which is commercially available from Henkel Corporation of Kankakee, Illinois.

⁴² POLYOX WSR-301 polyoxyethylene polymer which is commercially available from Union Carbide of Danbury, Connecticut.

⁴³ PolarTherm® PT 160 boron nitride powder particles which are commercially available from Advanced Ceramics Corporation of Lakewood, Ohio.

⁴⁴ ORPAC BORON NITRIDE RELEASECOAT-CONC boron nitride particles in aqueous dispersion which is commercially available from ZYP Coatings, Inc. of Oak Ridge, Tennessee.

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Aqueous forming size compositions A-D and Comparative Sample No. 1 were coated onto E-glass fiber strands. Each of the forming size compositions had about 2.5 weight percent solids. Each coated glass fiber strand was twisted to form a yarn and wound onto bobbins in a similar manner using conventional twisting equipment.

The yarns of Samples A-D, Comparative Sample No. 1 and a Comparative Sample No. 2⁴⁵ were evaluated for several physical properties, such as loss on ignition (LOI), air jet compatibility (Air Drag), Friction Force and broken filaments.

The average loss on ignition (weight percent of solids of the forming size composition divided by the total weight of the glass and dried forming size composition) of three trials of each Sample is set forth in Table 7.

Each yarn was evaluated for Air Drag Force or tension by feeding the yarn at a controlled feed rate of 274 meters (300 yards) per minute through a checkline tension meter, which applied a tension to the yarn, and a Ruti two millimeter diameter air nozzle at an air pressure of 310 kPa (45 pounds per square inch).

The Samples and Comparative Samples were also evaluated for Friction Force by applying a tension of about 30 grams to each yarn sample as the sample is pulled at a rate of 274 meters (300 yards) per minute through a pair of conventional tension measurement devices having a stationary chrome post of about 5 centimeters (2 inches) diameter mounted therebetween to displace the yarn about 5 centimeters from a straight line path between the tension measurement devices. The difference in force in grams is set forth in Table 7 below. The Friction Force test is intended to simulate the frictional forces to which the yarn is subjected during weaving operations.

⁴⁵ PPG Industries, Inc.'s 1383 commercially available fiber glass yarn product.

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Each sample and comparative sample was also evaluated for broken filaments using an abrasion tester. Two hundred grams of tension were applied to each test sample as each test sample was pulled at a rate of 0.46 meters (18 inches) per minute for five minutes through an abrasion testing apparatus. Two test runs of each sample and comparative sample were evaluated and the average of the number of broken filaments is reported in Table 7 below. The abrasion tester consisted of two parallel rows of steel reeds, each row being positioned about 1 inch apart. Each test yarn sample was threaded between two adjacent reeds of the first row of reeds, then threaded between two adjacent reeds of the second row of reeds, but displaced a distance of one-half inch between the rows of reeds. The reeds were displaced back and forth over a four inch length in a direction parallel to the direction of yarn travel at a rate of 240 cycles per minute. The results of Air Drag Force, Friction Force and Broken Filaments Under Abrasion for Samples A-D and the comparative samples are set forth in Table 7 below.

Table 7

	Sample					
	A	B	C	D	Comparative Sample No. 1	Comparative Sample No. 2
LOI (weight percent)	0.35	0.30	0.52	0.40	0.33	0.75
Air Drag (grams)	68.5	84.9	37.3	47.1	36.4	19.0
Friction force (grams)	24.7	18.3	-	-	23.9	38.1
Number of broken filaments per yard of yarn	2.0	1.0	-	-	3.8	1.0

As shown in Table 7, Samples A and B, which are coated with sizing compositions containing boron nitride according to the present invention, had few broken filaments, low frictional force and higher air drag values when compared to the Comparative Samples. Samples C and D also had higher air drag values than the Comparative Samples. The air drag test is a relative

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test intended to simulate the weft insertion process of an air jet loom in which the yarn is conveyed across the loom by air jet propulsion. Yarns which are more readily filamentized by the air jet provide greater surface area for air jet propulsion, which can facilitate yarn travel across the loom and increase productivity. The air drag values for Samples A-D (samples prepared according to the present invention) are higher than those of the Comparative Samples, which indicates superior air jet compatibility.

EXAMPLE 5

10 Each of the components in the amounts set forth in Table 8 were mixed to form aqueous forming size compositions E, F, G and H according to the present invention and the Comparative Sample in a similar manner to that discussed above. Less than about 1 weight percent of acetic acid on a total weight basis was included in each composition.

15 Each of the aqueous forming size compositions of Table 8 were coated onto G-75 E-glass fiber strands. Each of the forming size compositions had between about 6 and about 25 weight percent solids.

Table 8

COMPONENT	WEIGHT PERCENT OF COMPONENT ON TOTAL SOLIDS BASIS				
	Sample No.				
	E	F	G	H	Comp. Sample
Epoxy film-forming polymer ⁴⁶	16.12	63.54	16.12	63.54	60.98
Polyvinyl pyrrolidone ⁴⁷	1.31	5.18	1.31	5.18	4.97
Polyoxyethylated vegetable oil ⁴⁸	1.63	6.44	1.63	6.44	6.18
Ethoxylated octylphenoxyethanol ⁴⁹	1.63	6.44	1.63	6.44	6.18
polyethylene glycol monolaurate ester ⁵⁰	0.79	3.11	0.79	3.11	2.98
Epoxy-functional organo silane coupling agent ⁵¹	3.17	12.51	3.17	12.51	12.00
Organic lubricant ⁵²	0.40	1.56	0.40	1.56	1.50
polyethylene emulsion ⁵³	0	0	0	0	4.61
Boron nitride powder particles ⁵⁴	74.78	1.00	0	0	0
Boron nitride particles in aqueous suspension ⁵⁵	0	0	74.78	1.00	0

- Each coated glass fiber strand was twisted to form yarn and wound onto bobbins in a similar manner using conventional twisting equipment. The
- 5 yarns of Samples F and H exhibited minimal sizing shedding during twisting and the yarns of Samples E and G exhibited severe sizing shedding during twisting.

⁴⁶ EPON 826 which is commercially available from Shell Chemical of Houston, Texas.

⁴⁷ PVP K-30 polyvinyl pyrrolidone which is commercially available from ISP Chemicals of Wayne, New Jersey.

⁴⁸ ALKAMULS EL-719 polyoxyethylated vegetable oil which is commercially available from Rhone-Poulenc.

⁴⁹ IGEPAL CA-630 ethoxylated octylphenoxyethanol which is commercially available from GAF Corporation of Wayne, New Jersey.

⁵⁰ KESSCO PEG 600 polyethylene glycol monolaurate ester which is commercially available from Stepan Company of Chicago, Illinois.

⁵¹ A-187 gamma-glycidoxypolytrimethoxysilane which is commercially available from OSI Specialties, Inc. of Tarrytown, New York.

⁵² EMERY® 6717 partially amidated polyethylene imine which is commercially available from Henkel Corporation of Kankakee, Illinois.

⁵³ Protolube HD high density polyethylene emulsion which is commercially available from Sybron Chemicals of Birmingham, New Jersey.

⁵⁴ PolarTherm® PT 160 boron nitride powder particles which are commercially available from Advanced Ceramics Corporation of Lakewood, Ohio.

⁵⁵ ORPAC BORON NITRIDE RELEASECOAT-CONC boron nitride particles in aqueous dispersion which is commercially available from ZYP Coatings, Inc. of Oak Ridge, Tennessee.

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The yarns of Samples E-H and Comparative Sample were evaluated for Air Drag in a similar manner to Example 4 above, except that the Air Drag values were determined for two bobbin samples at the pressures indicated in Table 9. Each yarn was evaluated for average number of broken filaments
5 per 1200 meters of yarn at 200 meters per minute using a Shirley Model No. 84 041L broken filament detector, which is commercially available from SDL International Inc. of England. These values represent the average of measurements conducted on four bobbins of each yarn. The broken filament values are reported from sections taken from a full bobbin, 136 grams (3/10
10 pound) and 272 grams (6/10 pound) of yarn unwound from the bobbin.

Each yarn was also evaluated for Gate Tension testing are set forth in Table 9 below. The number of broken filaments measured according to the Gate Tension Method is determined by unwinding a sample of yarn from a bobbin at 200 meters/minute, threading the yarn through a series of 8 parallel
15 ceramic pins and passing the yarn through the Shirley broken filament detector discussed above to count the number of broken filaments.

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TABLE 9

NUMBER OF BROKEN FILAMENTS PER METER OF YARN		Sample E	Sample F	Sample G	Sample H	Comp. Sample
full bobbin		0.887	0.241	greater than 10	0.065	0.192
136 grams (3/10 pound)		0.856	0.017	greater than 10	0.013	0.320
272 grams (6/10 pound)		0.676	0.030	greater than 10	0.101	0.192
GATE TENSION (number of hairs per meter)						
Gate 2		-	0.039	-	0.0235	0.721
Gate 3		-	0.025	-	0.028	0.571
Gate 4		-	0.0125	-	0.068	0.4795
Gate 5		-	0.015	-	0.093	0.85
Gate 6		-	0.0265	-	0.118	0.993
Gate 7		-	0.0695	-	0.31	1.0835
Gate 8		-	0.117	-	0.557	1.81
AIR DRAG (grams)						
25 psi	Bobbin 1	-	10.420	-	10.860	11.610
	Bobbin 2	-	10.600	-	7.850	11.610
30 psi	Bobbin 1	-	11.690	-	12.500	13.680
	Bobbin 2	-	12.200	-	8.540	13.850
35 psi	Bobbin 1	-	13.490	-	14.030	15.880
	Bobbin 2	-	13.530	-	9.570	15.630
40 psi	Bobbin 1	-	14.740	-	14.110	17.560
	Bobbin 2	-	14.860	-	11.010	17.610
45 psi	Bobbin 1	-	16.180	-	16.390	19.830
	Bobbin 2	-	16.680	-	12.700	18.950
50 psi	Bobbin 1	-	17.510	-	19.280	22.410
	Bobbin 2	-	17.730	-	14.000	20.310
55 psi	Bobbin 1	-	19.570	-	23.350	29.350
	Bobbin 2	-	19.660	-	20.250	26.580

While the test results presented in Table 9 appear to indicate that Samples E-H according to the present invention had generally higher abrasion resistance than the Comparative Sample, it is believed that these results are not conclusive since it is believed that a polyethylene emulsion component of the Comparative Sample, which was not present in Samples E-H, contributed to abrasive properties of the yarn.

EXAMPLE 6

Five layers of ADFLO-C™ needled chopped glass fiber mat, which is commercially available from PPG Industries, Inc., were stacked to form a mat having a surface weight of about 4614 grams per square meter (15 ounces per square foot). The thickness of each sample was about 25 millimeters (about 1 inch). Four eight-inch square samples of this mat were heated to a temperature of about 649°C (about 1200°F) to remove essentially all of the sizing components from the samples.

Two uncoated samples were used as comparative samples. The other two samples were dipped and saturated in a bath of an aqueous coating composition consisting of 1150 milliliters of ORPAC BORON NITRIDE RELEASECOAT-CONC (25 weight percent boron nitride particles in an aqueous dispersion) and 150 milliliters of a 5 weight percent aqueous solution of A-187 gamma-glycidoxypyrtrimethoxysilane. The total solids of the aqueous coating composition was about 18.5 weight percent. The amount of boron nitride particles applied to each mat sample was about 120 grams. The coated mat samples were dried in air overnight at a temperature of about 25°C and heated in an oven at about 150°C for about 3 hours.

Each set of samples was evaluated for thermal conductivity and thermal resistance in air at temperatures of about 300K (about 70°F) according to ASTM Method C-177, which is hereby incorporated by reference. The values for thermal conductivity and thermal resistance for each sample are set forth in Table 10 below.

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Table 10

	Sample	
	X	Comp. Sample
Thickness (inches)	1.09	1.0
(centimeters)	2.77	2.54
Temperature (°F)	75.62	74.14
(°C)	24.23	23.41
Thermal conductivity		
Btu inches per hour square feet°F	0.373	0.282
Watts per meter K	0.054	0.041
Thermal resistance		
Hour square feet °F per BTU	2.92	3.55
meter ² K per Watts	0.515	0.626

Referring to Table 10, the thermal conductivity at a temperature about 300K of the test sample coated with boron nitride particles according to the present invention was greater than the thermal conductivity of the Comparative Sample which was not coated with boron nitride particles.

EXAMPLE 7

Filament wound cylindrical composites were prepared from samples of G-75 yarn coated with sizing G of Example 5 above and 1062 glass fiber yarn which is commercially available from PPG Industries, Inc. The cylinders were prepared by drawing eight ends of yarn from a yarn supply, coating the yarn with the matrix materials set forth below, and filament winding the yarn into a cylindrical shape using a conventional filament winding apparatus. Each of the cylinders was 12.7 centimeters (5 inches) high, had an internal diameter of 14.6 centimeters (5.75 inches) and a wall thickness of 0.635 centimeters (0.25 inches).

The matrix materials were a mixture of 100 parts EPON 880 epoxy resin (commercially available from Shell Chemical), 80 parts AC-220J methyl

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tetrahydro phthalic anhydride (commercially available from Anhydrides and Chemicals, Inc. of Newark, New Jersey), and 1 part ARALDITE® DY 062 benzyl dimethyl amine accelerator (commercially available from Ciba-Geigy). The filament wound cylinders were cured for two hours at 100°C and then for
5 three hours at 150°C.

The radial thermal diffusivity (thermal conductivity/(heat capacity x density)) of each test sample in air was determined by exposing one side of the cylinder wall of the sample to a 6.4 kJ flash lamp and sensing the temperature change on the opposite side of the wall using a CCD array
10 infrared camera at a rate of up to 2000 frames per second. Thermal diffusivity values were also determined along a length of the yarn (circumferential) and along a length or height of the cylinder (axial). The test results are set forth below in Table 11.

15

Table 11

	Thermal Diffusivity (mm ² /sec)		
	radial	axial	circumferential
Sample	0.37	0.33	0.49
Comparative Sample	0.38	0.38	0.57

Referring to Table 11, the values of thermal diffusivity for the test sample (which was coated with a small amount of boron nitride) are less than those of the comparative sample, which was not coated with boron nitride.
20 Air voids in the filament wound cylinder and the small sample area tested are factors which may have influenced these results.

From the foregoing description, it can be seen that the present invention provides glass fiber strands having an abrasion-resistant coating
25 which are compatible with a variety of polymeric matrix materials. These strands can be twisted or chopped, formed into a roving, chopped mat or

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continuous strand mat or woven or knitted into a fabric for use in a wide variety of applications, such as reinforcements for composites such as printed circuit boards. The inorganic fillers provide the coated fiber strands with physical properties which are comparable to those of conventional coated

5 fiber strands at reduced cost.

It will be appreciated by those skilled in the art that changes could be made to the embodiments described above without departing from the broad inventive concept thereof. It is understood, therefore, that this invention is not limited to the particular embodiments disclosed, but it is intended to cover

10 modifications which are within the spirit and scope of the invention, as defined by the appended claims.

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THEREFORE, WE CLAIM:

1. A coated fiber strand comprising at least one glass fiber at least partially coated with a dried residue of an aqueous sizing composition
5 comprising greater than 20 weight percent on a total solids basis of inorganic solid particles which have a hardness which does not exceed a hardness of the at least one glass fiber.
2. The coated fiber strand according to claim 1, wherein the
10 minimum average particle size of the inorganic solid particles is at least 3 micrometers.
3. The coated fiber strand according to claim 2, wherein the
15 minimum average particle size of the inorganic solid particles ranges from 3 micrometers to less than about 1000 micrometers.
4. The coated fiber strand according to claim 1, wherein the
minimum average particle size of the inorganic solid particles is at least about
5 micrometers.
20
5. The coated fiber strand according to claim 4, wherein the
minimum average particle size of the inorganic particles ranges from about 5
micrometers to less than about 1000 micrometers
- 25 6. The coated fiber strand according to claim 1, wherein the
hardness value of the inorganic solid particles is less than or equal to the
hardness value of the at least one glass fiber.

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7. The coated fiber strand according to claim 1, wherein the inorganic solid particles have a Mohs' hardness ranging from about 1 to about 6.

5 8. The coated fiber strand according to claim 1, wherein the inorganic solid particles are formed from at least one inorganic material selected from the group consisting of ceramic materials and metallic materials.

10 9. The coated fiber strand according to claim 8, wherein the inorganic solid particles are formed from at least one ceramic material selected from the group consisting of metal nitrides, metal oxides, metal carbides, metal sulfides, metal borides, metal silicates, metal carbonates and mixtures thereof.

15 10. The coated fiber strand according to claim 9, wherein the inorganic solid particles are formed from a metal nitride which is hexagonal crystal structure boron nitride.

20 11. The coated fiber strand according to claim 1, wherein the inorganic solid particles are hydrophilic and which upon exposure to water absorb and retain water in interstices within the hydrophilic solid particles.

25 12. The coated fiber strand according to claim 8, wherein the solid particles are formed from at least one metallic material selected from the group consisting of graphite, molybdenum, platinum, palladium, nickel, aluminum, copper, gold, iron, silver and mixtures thereof.

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13. The coated fiber strand according to claim 1, wherein the aqueous sizing composition is essentially free of hydratable inorganic solid particles.

5 14. The coated fiber strand according to claim 1, wherein the inorganic solid particles comprise greater than 20 to about 99 weight percent of the sizing composition on a total solids basis.

10 15. The coated fiber strand according to claim 14, wherein the inorganic solid particles comprise at least about 25 weight percent of the sizing composition on a total solids basis.

15 16. The coated fiber strand according to claim 15, wherein the inorganic solid particles comprise greater than about 50 weight percent of the sizing composition on a total solids basis.

20 17. The coated fiber strand according to claim 1, wherein the sizing composition further comprises a polymeric film-forming material is selected from the group consisting of thermosetting materials, thermoplastic materials, starches and mixtures thereof.

18. The coated fiber strand according to claim 1, wherein the sizing composition further comprises a glass fiber coupling agent.

25 19. The coated fiber strand according to claim 1, wherein at least one of the at least one glass fiber is formed from a fiberizable material selected from the group consisting of non-glass inorganic materials, natural materials, organic polymeric materials and combinations thereof.

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20. The coated fiber strand according to claim 1, wherein the at least one glass fiber is selected from the group consisting of E-glass fibers, D-glass fibers, S-glass fibers, Q-glass fibers, E-glass derivative fibers, and combinations thereof.
- 5
21. The coated fiber strand according to claim 20, wherein the at least one glass fiber is an E-glass fiber.
22. The coated fiber strand according to claim 20, wherein the at least one glass fiber is an E-glass derivative fibers.
- 10
23. A coated fiber strand comprising at least one glass fiber, the strand having (1) a primary layer of a dried residue of a sizing composition applied to at least a portion of surfaces of at least one glass fiber and (2) a secondary layer of an aqueous secondary coating composition applied over at least a portion of the primary layer, the secondary coating composition comprising greater than 20 weight percent on a total solids basis of inorganic solid particles.
- 15
24. The coated fiber strand according to claim 23, wherein the at least one glass fiber is selected from the group consisting of E-glass fibers, D-glass fibers, S-glass fibers, Q-glass fibers, E-glass derivative fibers, and combinations thereof.
- 20
25. The coated fiber strand according to claim 24, wherein the at least one glass fiber is an E-glass fiber.
- 25
26. The coated fiber strand according to claim 24, wherein the at least one glass fiber is an E-glass derivative fibers.

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27. A coated fiber strand comprising at least one glass fiber, the strand having (1) a primary layer of a dried residue of a sizing composition applied to at least a portion of surfaces of the at least one glass fiber; (2) a
5 secondary layer of a secondary coating composition applied over at least a portion of the primary layer, the secondary coating composition comprising a polymeric material; and a tertiary layer comprising greater than 20 weight percent on a total solids basis of powdered inorganic solid particles applied over at least a portion of the secondary layer.

10

28. The coated fiber strand according to claim 27, wherein the at least one glass fiber is selected from the group consisting of E-glass fibers, D-glass fibers, S-glass fibers, Q-glass fibers, E-glass derivative fibers, and combinations thereof.

15

29. The coated fiber strand according to claim 28, wherein the at least one glass fiber is an E-glass fiber.

30. The coated fiber strand according to claim 28, wherein the at
20 least one glass fiber is an E-glass derivative fibers.

31. A reinforced polymeric composite comprising:

(a) a coated fiber strand comprising at least one glass fiber at least partially coated with a dried residue of an aqueous sizing composition
25 comprising greater than 20 weight percent on a total solids basis of inorganic solid particles which have a hardness which does not exceed a hardness of the at least one glass fiber; and

(b) a polymeric matrix material.

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32. The reinforced polymeric composite according to claim 31, wherein the at least one glass fiber is selected from the group consisting of E-glass fibers, D-glass fibers, S-glass fibers, Q-glass fibers, E-glass derivative fibers, and combinations thereof.

5

33. A fabric comprising a coated fiber strand comprising a coated fiber strand comprising at least one glass fiber at least partially coated with a dried residue of an aqueous sizing composition comprising greater than 20 weight percent on a total solids basis of inorganic solid particles which have a
10 hardness which does not exceed a hardness of the at least one glass fiber.

34. The fabric according to claim 33, wherein the at least one glass fiber is selected from the group consisting of E-glass fibers, D-glass fibers, S-glass fibers, Q-glass fibers, E-glass derivative fibers, and combinations
15 thereof.

35. An electronic support comprising:

(a) a fabric comprising a coated fiber strand comprising at least one glass fiber at least partially coated with a dried residue of an aqueous sizing
20 composition comprising greater than 20 weight percent on a total solids basis of inorganic solid particles which have a hardness which does not exceed a hardness of the at least one glass fiber; and

(b) a layer of a polymeric matrix material applied over at least a portion of the fabric.

25

36. The electronic support according to claim 35, wherein the at least one glass fiber is selected from the group consisting of E-glass fibers, D-glass fibers, S-glass fibers, Q-glass fibers, E-glass derivative fibers, and combinations thereof.

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37. The electronic support according to claim 35 wherein the support is a first, second or third level package.

- 5 38. An electronic circuit board comprising:
- (a) an electronic support comprising:
- (i) a fabric comprising coated fiber strand comprising at least one glass fiber at least partially coated with a dried residue of an aqueous sizing composition comprising greater than 20 weight percent on a
- 10 total solids basis of inorganic solid particles which have a hardness which does not exceed a hardness of the at least one glass fiber; and
- (ii) a layer of a polymeric matrix material applied over at least a portion of the fabric; and
- (b) an electrically conductive layer positioned adjacent to selected
- 15 portions of selected sides of the electronic support.

39. The electronic circuit board according to claim 38, wherein the at least one glass fiber is selected from the group consisting of E-glass fibers, D-glass fibers, S-glass fibers, Q-glass fibers, E-glass derivative fibers, and

20 combinations thereof.

40. The electronic circuit board according to claim 38 further comprising at least one aperture extending through at least a portion of the circuit board.

25

41. The electronic circuit board according to claim 38 wherein the support is a first, second or third level package.

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42. An electronic support comprising:
- (a) a first composite layer comprising:
- (i) a fabric comprising a coated fiber strand comprising at least one glass fiber at least partially coated with a dried residue of an aqueous sizing composition comprising greater than 20 weight percent on a total solids basis of inorganic solid particles which have a hardness which does not exceed a hardness of the at least one glass fiber; and
- (ii) a layer of a polymeric matrix material applied over at least a portion of the fabric; and
- (b) a second composite layer different from the first composite layer.

43. The electronic support according to claim 42, wherein the at least one glass fiber is selected from the group consisting of E-glass fibers, D-glass fibers, S-glass fibers, Q-glass fibers, E-glass derivative fibers, and combinations thereof.

44. The electronic support according to claim 42 wherein the support is a first, second or third level package.

45. An electronic circuit board comprising:
- (a) an electronic support comprising:
- (i) a first composite layer comprising:
- (1) a fabric comprising coated fiber strand comprising at least one glass fiber at least partially coated with a dried residue of an aqueous sizing composition comprising greater than 20 weight percent on a total solids basis of inorganic solid particles which have a hardness which does not exceed a hardness of the at least one glass fiber; and

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(2) a layer of a polymeric matrix material applied over at least a portion of the fabric; and

(ii) a second composite layer different from the first composite layer; and

5 (b) an electrically conductive layer positioned adjacent to selected portions of selected sides of the first and/or second composite layers.

46. The electronic circuit board according to claim 45, wherein the at least one glass fiber is selected from the group consisting of E-glass fibers,
10 D-glass fibers, S-glass fibers, Q-glass fibers, E-glass derivative fibers, and combinations thereof.

47. The electronic circuit board according to claim 45 further comprising at least one aperture extending through at least a portion of the
15 circuit board.

48. The electronic circuit board according to claim 45 wherein the support is a first, second or third level package.

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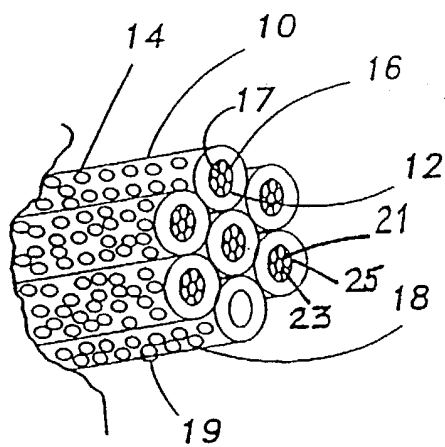


FIG. 1

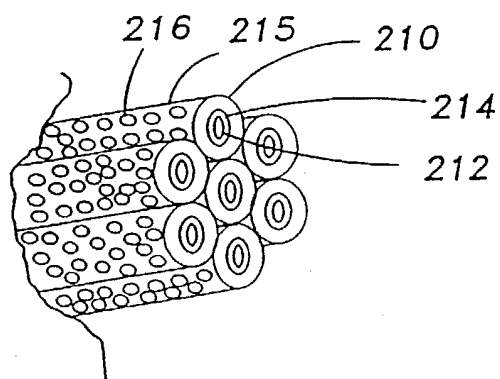


FIG. 2

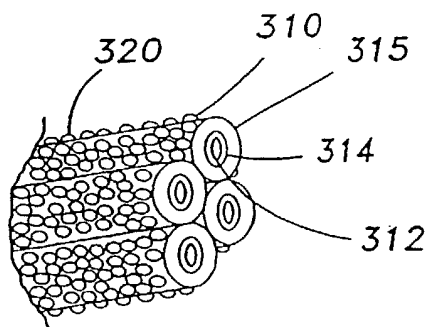


FIG. 3

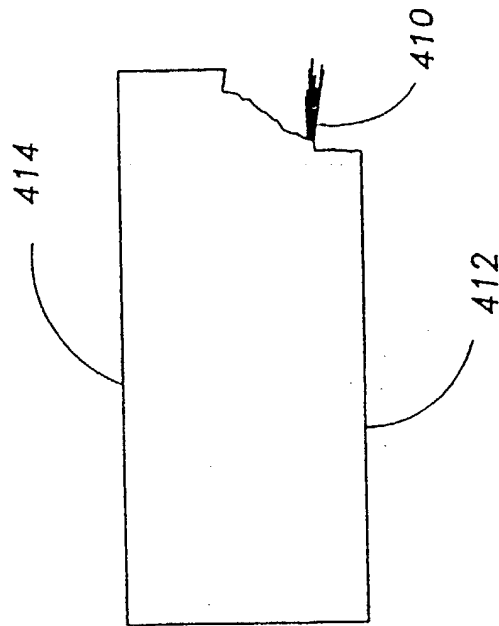


FIG. 4

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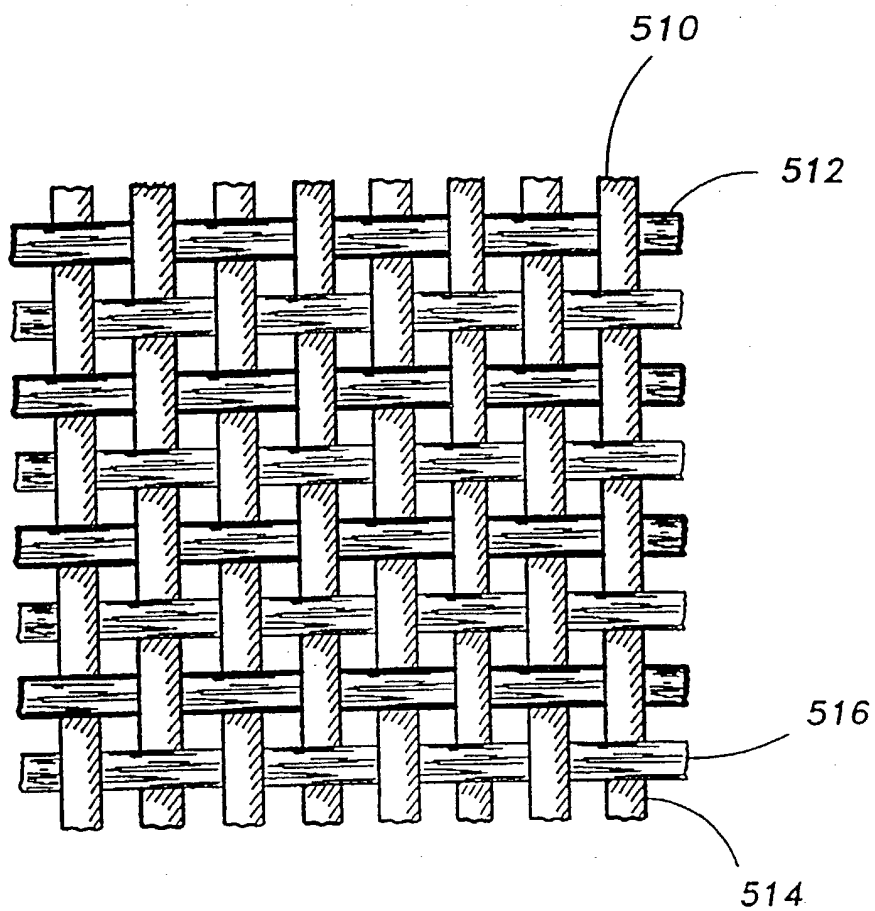


FIG. 5

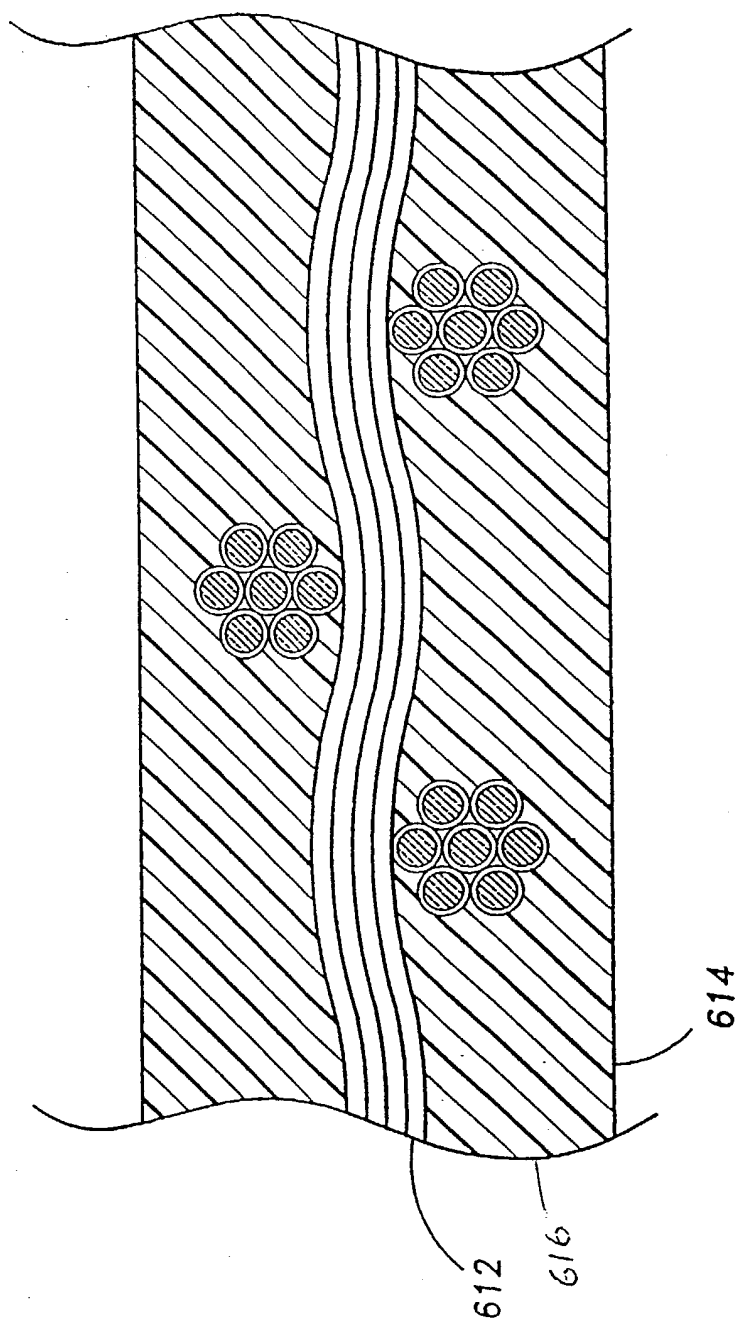


FIG. 6

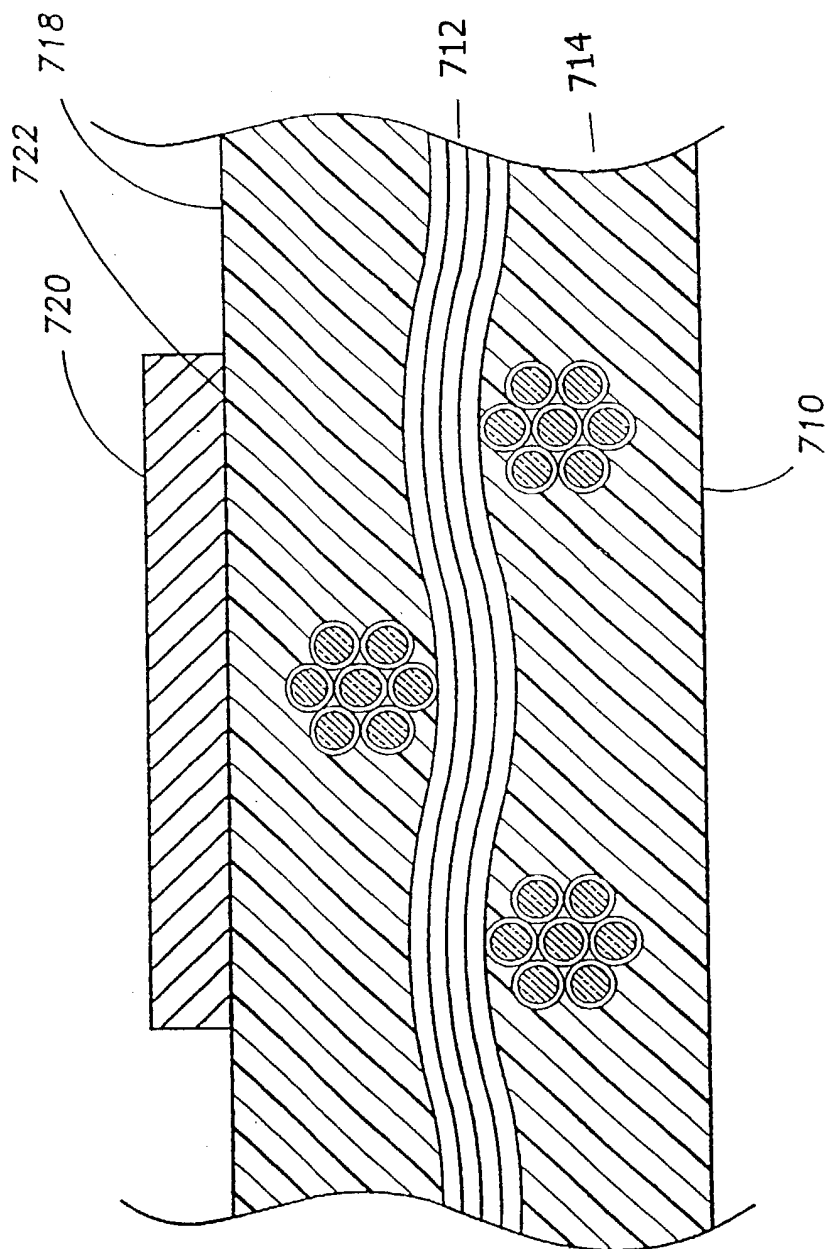


FIG. 7

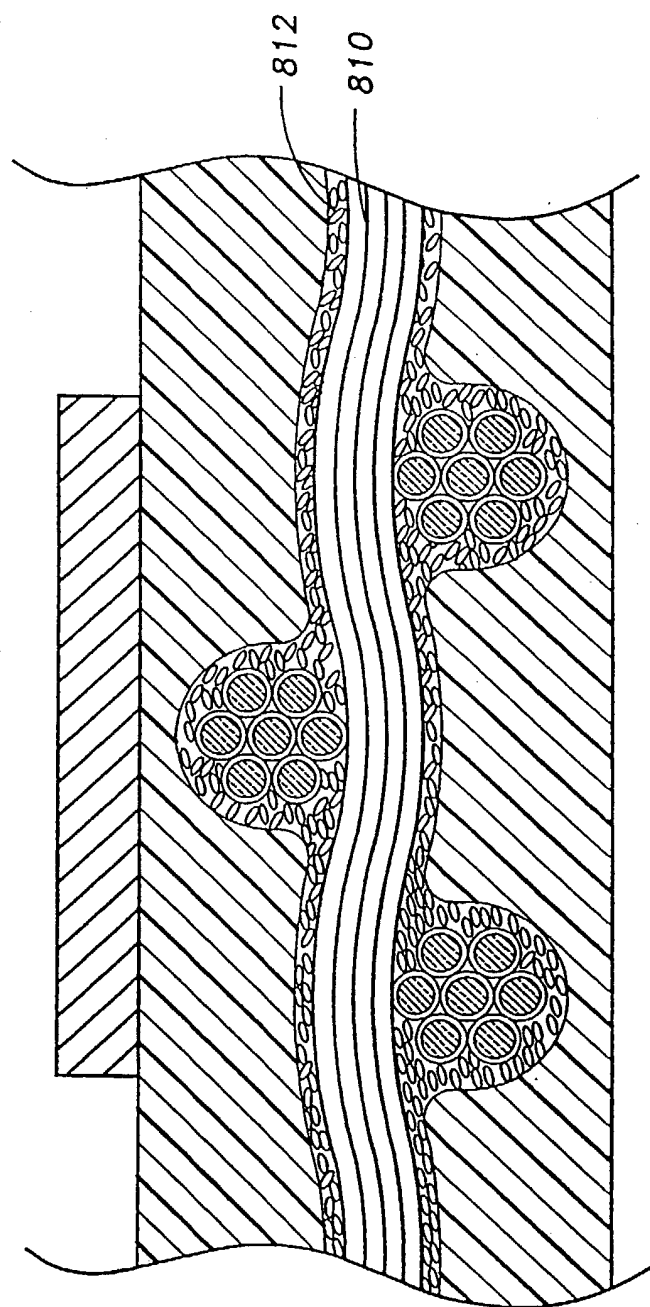


FIG. 8

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/04057

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C03C25/02 C08J5/08 H05K1/03

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C03C C08J H05K F16D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 90 01860 A (TELDIX GMBH) 22 February 1990 see claims ---	1-48
A	US 3 312 569 A (T.E. PHILIPPS ET AL.) 4 April 1967 cited in the application see claims ---	1-34
A	US 5 217 778 A (G.J. LACHASSE) 8 June 1993 cited in the application see abstract ---	1-34
A	WO 96 39364 A (PPG INDUSTRIES INC.) 12 December 1996 see page 5, line 1 - line 13 ---	1-48
-/--		



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

° Special categories of cited documents:

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

18 June 1999

Date of mailing of the international search report

02/07/1999

Name and mailing address of the ISA

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Reedijk, A

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>DATABASE WPI Section Ch, Week 9706 Derwent Publications Ltd., London, GB; Class A85, AN 97-060830 XP002106571 & JP 08 309928 A (HITACHI CHEM CO LTD) , 26 November 1996 see abstract</p>	1-48
A	<p>DATABASE WPI Section Ch, Week 9728 Derwent Publications Ltd., London, GB; Class A18, AN 97-306602 XP002106572 & JP 09 118759 A (MATSUSHITA ELECTRIC WORKS LTD), 6 May 1997 see abstract</p>	1-48
A	<p>PATENT ABSTRACTS OF JAPAN vol. 014, no. 423 (C-0757), 12 September 1990 & JP 02 160944 A (NITTO BOSEKI CO LTD), 20 June 1990 see abstract</p>	1-48
T	<p>DATABASE INSPEC INSTITUTE OF ELECTRICAL ENGINEERS, STEVENAGE, GB Inspec No. 6242125, NOVICH B E: "Hybon RCY yarns: a laminate reinforcement developed for printed circuit boards" XP002106570 see abstract & CIRCUITREE, MARCH 1999, CIRCUITREE, USA, vol. 12, no. 3, page 44, 46, 51 ISSN 1059-843X</p>	1-48

Information on patent family members

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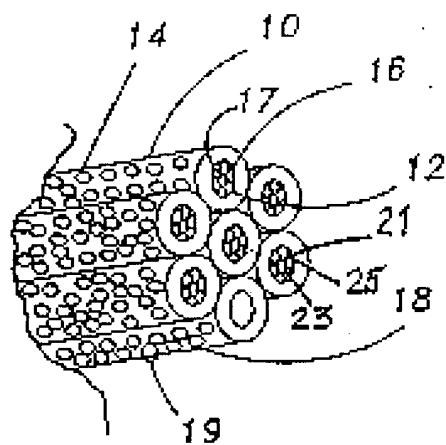


FIG. 1

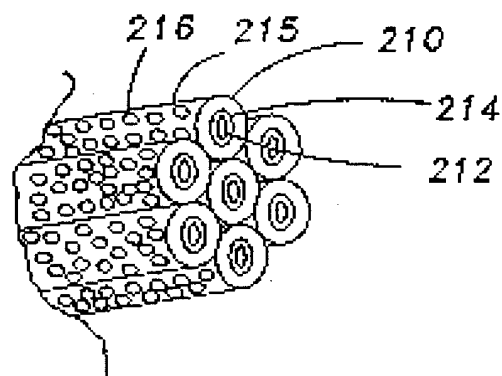


FIG. 2

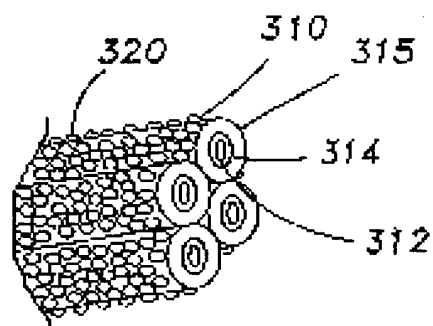


FIG. 3

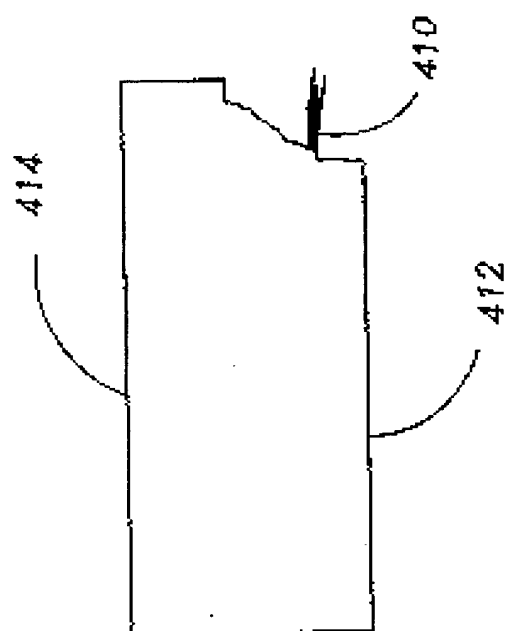


FIG. 4

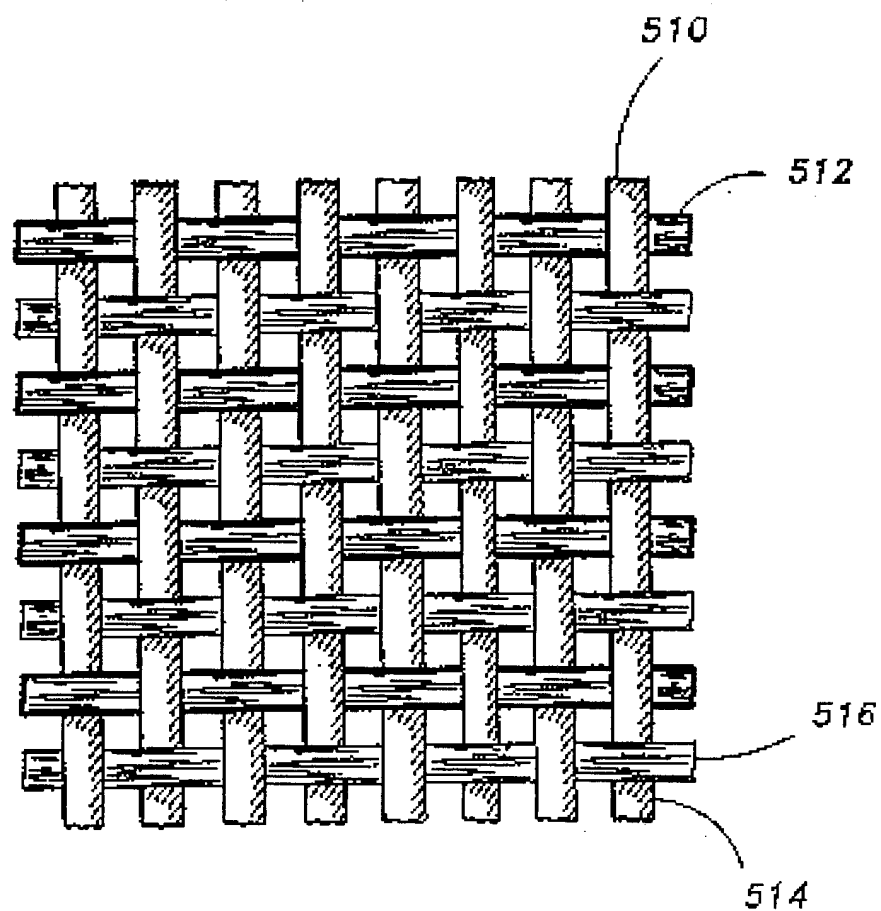


FIG. 5

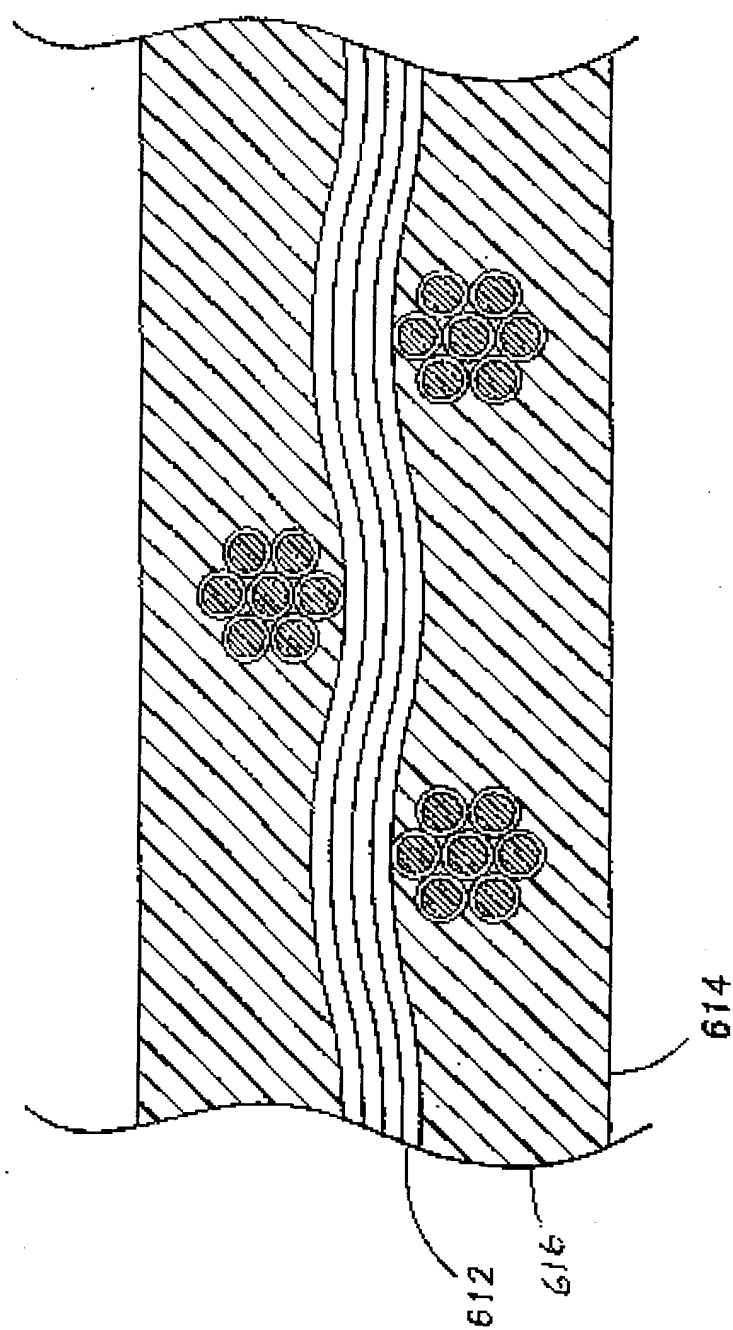


FIG. 6

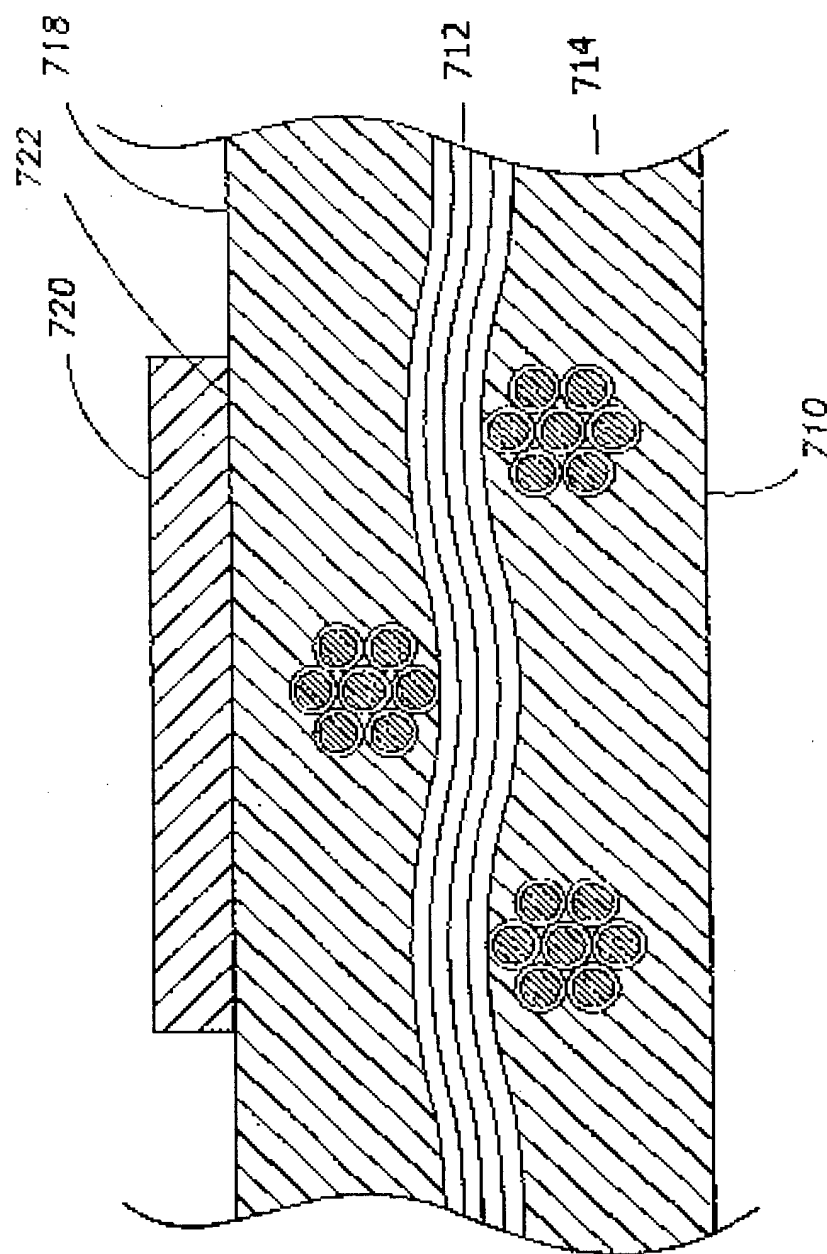


FIG. 7

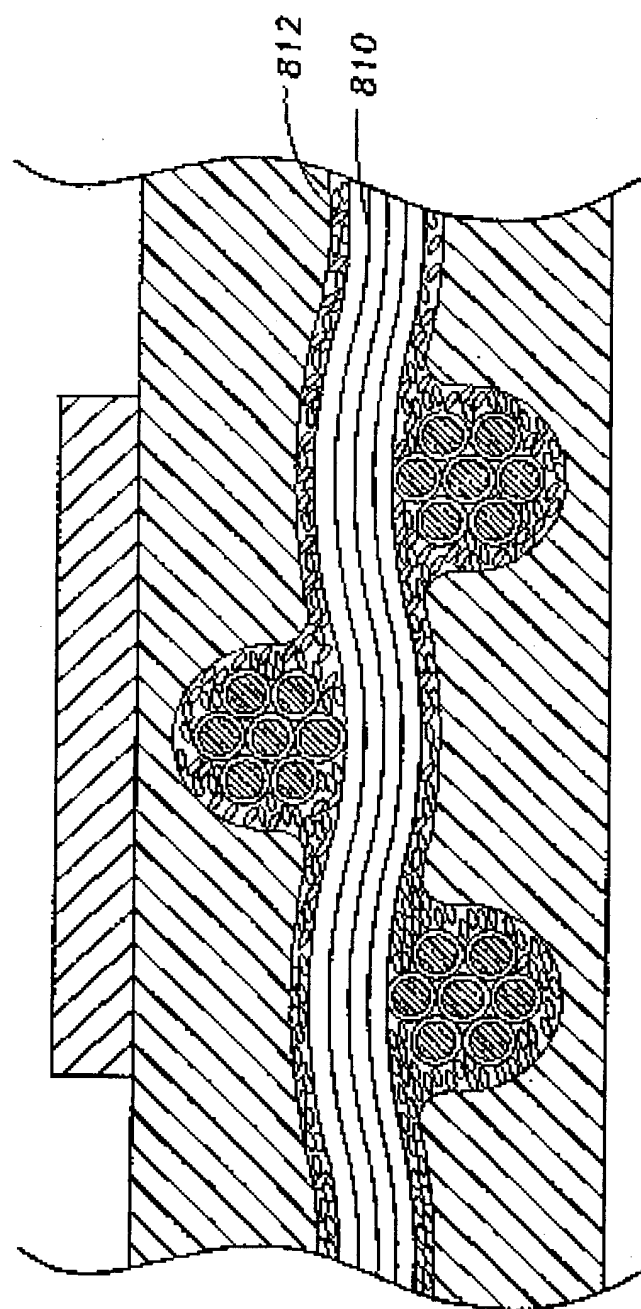


FIG. 8